Commentary

RESEARCH IN SCHOOLS

THE recognition of the shortage of science teachers in schools and the increasing demands in scientific manpower emphasize the need to encourage interest in experimental science at an early age. It is most important that minds naturally suited for such a career should apprehend the adventure of discovery in their formative years. Learning in schools, of necessity, involves the absorption of a great deal of mere information. If the learning can be associated with discovery, if the development of the pattern of thought we call knowledge can be experienced, not only is it more readily apprehended but it becomes the more exciting. Anything therefore which can encourage the spirit of research in the schools is calculated to bring far-reaching benefits. Credit for initiating help for research in schools belongs to Dr. C. G. WILLIAMS and Shell Research Ltd, who for some years assisted research projects in seven schools both financially and in other ways.

Not the least important help is expert advice in the projects which teachers wish to plan and to undertake. In the belief that, with the help, of its Fellows and other experts with whom it is in contact, the Royal Society was in an especially favourable position to furnish such advice, the Council of the Royal Society set up a Committee under the Chairmanship of the Biological Secretary in March 1957 to assist research in schools. On this Committee the Royal Society is represented by three of its Fellows and Dr. C. G. WILLIAMS serves with three other members representing the Science Masters' Association.

It should be stressed that the primary aim of this scheme is not so much to further particular research projects for their own sake, however admirable these objectives might be, as to promote investigations in schools which are likely to have a *direct* influence on the pupils as well as benefitting the teacher and thus the pupils *indirectly*. Consequently the Committee considers with especial sympathy projects in which the schoolboys and schoolgirls can themselves participate. A project which a master could only pursue in vacations or at home may be a very desirable one but its influence on those he instructs would be indirect. Owing to the limited funds at its disposal, the Committee would probably regard such a proposal as less eligible for financial assistance and perhaps beyond the range of what it could usefully support—though, of course, appropriate as a subject for advice.

The many obstacles that militate against the conduct of research in schools are fully appreciated by the Committee. Of these, the lack of requisite time free from routine duties is probably the most difficult to overcome where a shortage of staff is acute and tribute should be paid to those who carry on investigations despite difficulties. Facilities such as the provision of essential apparatus and access to the relevant literature are however made available more readily. In a university department or in a research institution anyone carrying out an original investigation has the stimulus of contact with other minds, similarly occupied and trained in the same or cognate subjects. The science teacher is often comparatively isolated without any scientific colleague with whom to discuss his problems and difficulties. The Royal Society scheme aims to minimize this most important difficulty by an expert adviser for each project. It is a pleasure, though not an unexpected one, to record the willingness with which Fellows and other specialists have given of their time. This advice, which is usually coupled with personal interviews, is given on projects in hand, on research programmes and on facilities which might suitably be provided by the Committee. It is normally expected that teachers will themselves suggest projects that attract their interest and for which they have the environment to pursue profitably.

In the first year of the Committee's activities, advice was given to fifty-seven science teachers whilst in the past year forty-four schools were carrying out research projects for which the Committee had been the means of providing advice and facilities. In a number of instances financial help was also furnished, amounting in all during the twelve months to over £2,000.

It is hoped that the advice and assistance which the Committee sponsors will provide help and encouragement to those science teachers who are carrying out investigations. Furthermore this will make manifest that 'The Royal Society of London for Improving Natural Knowledge'—to give its full title—is conscious that science teachers and their pupils can make contributions of real worth to the advancement of learning and can themselves indeed foster the spirit of scientific observation and experiment.

E. J. SALISBURY

MODERN DYES

CLIFFORD PAINE

Director, Imperial Chemical Industries Ltd

The author outlines the development of modern dyeing techniques and describes the different types of dyes in use at present. The article is taken from the Sir William Pope Memorial Lecture given by Mr Paine at the Royal Society of Arts on February 3rd, 1960.

THE contemporary palette of synthetic dyes provides a comprehensive range of shades and properties which makes them suitable for a wide diversity of uses. Indeed, where a particular combination of shades and properties is required for a specific purpose there is usually freedom of choice among several candidates. There are currently two to three thousand commercially useful dyes, of which some two hundred or so can be said to be of major importance by virtue of unique shades or outstanding properties.

Underlying this profusion of colour is an intricate and fascinating pattern of organic chemistry. Nevertheless, it is not intended to deal comprehensively and in detail with the chemistry of modern dyes, but to examine the emergence of certain general concepts about the structure and behaviour of dyes and the impact of these concepts on modern dyeing technology. We can then consider in more detail a few modern dyes which embody some of the general concepts we have elucidated.

The dyes which are of major importance to the modern dyer are not all of recent discovery. *Indanthrone*, a blue dyestuff of outstanding fastness to light, was discovered and commercialized as early as 1901 and is still of prime importance. On the other hand, the so called reactive dyes which embody new principles and which are rapidly becoming major products have only been discovered within the last four or five years.

By 1880 the discovery of the azo dyes had widened the range of available shades to include yellows, oranges and scarlets, thus extending the dyers' palette beyond the blues and magentas of the earliest synthetic dyes. Almost all the dyes discovered in the second half of the last century could be dyed on silk or wool with relative ease from a water solution in presence of a small amount of acid. The emergence of the azo dyes in particular had a most profound effect on the future of wool dyeing. It came to be recognized that the sulphonic acid group which was a feature even of the early azo dyes conferred not only water-solubility on the dye but also considerably enhanced the affinity of the dye for the wool fibre.

The dyeing of cotton was, however, a much more difficult problem. All the early dyes had no direct affinity for the cotton fibre. They could only be fixed on cotton by metallic salts, tannic acid, and other devices designed to precipitate the dye in water in a soluble form within the fibre. These were devices which had previously been used in order to fix the natural vegetable dyes and also for producing colourations on fibres by the use of mineral pigments. Ideas about synthetic dyes for the dyeing of cotton were revolutionized by the discovery of *Congo Red* in 1884. It was found that this particular water soluble azo dye had the unique property of transferring itself from the aqueous dye bath to the cotton fibre and becoming firmly fixed there by the simple addition of common salt to the dye bath. Largely by trial and error, other dyestuff structures were found which also had this desirable property of direct affinity for cellulose.

Thus by the turn of the century it was recognized that the chemical structure of a dye had an important bearing on whether that dye would have a preferential affinity for animal fibres on the one hand or cellulosic fibres on the other, but it was not really until the 1930s that underlying causes of dyestuff affinity for fibres were studied in a quantitative way. This involved a study of dyeing as a physico-chemical mechanism; of how the dye transferred itself from water to the fibre surface and how the dye then moved within the fibre. These investigations were undoubtedly stimulated by the increasing knowledge of the structure of the natural fibres following the development of x-ray techniques. An additional stimulus to probe these problems of structure and affinity arose from the commercial development of cellulose acetate fibre after the First World War. It had been a shock to find that with few exceptions the vast array of available commercial dyes, admirable enough on natural fibres, just would not dye cellulose acetate at all.

The outstanding fastness both to light and to washing of indanthrone set up completely new standards of performance against which the new dyes of the future would have to measure. This so-called 'vat dye' had, however, offsetting disadvantages.

It is virtually insoluble in water and cannot be dyed in any of the usual ways. It can be reduced or 'vatted' by sodium hydrosulphite or similar reducing agents to give a water-soluble derivative which has a modest affinity for cotton and can therefore be applied from an aqueous dyebath and then the parent, blue indanthrone, can be regenerated within the cellulose fibre by re-oxidation. Thus, it can be dyed in a practical manner but by a multi-stage process and with some inconvenience.

Modern vat dyes now cover a wide range of shades with fastness properties approaching those of indanthrone. The criteria required of a modern vat dye are that it shall be easily 'vatted' or reduced, and that the reduction products which are known as 'leuco' compounds shall have a good solubility in water and a good affinity for cellulose. They are almost all highly coloured, and many vat dyes (for example, *Caledon Jade Green*) are of permanent importance in the modern dyers' armoury, colour fastness and attractive shades outweighing in some measure the inconvenience of application.

Fastness of Dyes

From time immemorial the dyers' preferred medium has been water. It is cheap, plentiful and convenient to handle. It is clear that the economics of dyeing will be most favourable with a dye which is readily soluble in water and yet will transfer from the water and fix itself on the fibre in one operation by modest applications of heat or by simple adjuvants. The early direct dyes, such as congo red, fulfilled these criteria admirably but nevertheless suffered from being relatively fugitive to light and only having moderate fastness to washing. There has therefore been a considerable urge to develop direct dyes with easy application and yet with fastness properties approximating more nearly to the vat dyes. Much success has been achieved. Considerable increase in light fastness has been brought about by the use of dyes containing copper or chromium to which reference is made later. Also, by careful attention to structural detail dyes with high intrinsic affinity have been obtained, with consequent improvement in standards of washing fastness. The modern dye chemist, however, has not been content to use higher direct affinity where the higher standards of washing fastness were required. The direct dyeing operation is to a greater or less extent reversible and washing fastness is by no means absolute. The possibility of producing a water-insoluble colouring matter within the fibre by first presenting it to the fibre in an intermediate and temporary soluble form has been a common concept, *e.g.* indanthrone and its leuco compound. A related method of achieving high standards of wet fastness is to synthesize a water-insoluble dye within the fibre itself from its intermediate components; for example, by soaking cotton fibre in an aqueous solution of a suitable naphthol or phenol and then reacting on this with a suitable diazonium solution, a water-insoluble azo pigment is produced within the interstices of the fibre itself.

Dispersed Dyes

The so-called dispersed dyes were designed in the first instance for the purpose of dyeing cellulose acetate. When cellulose acetate rayon was first commercially developed between the two wars it was found that the dyes available for use on natural fibres were of little or no value for colouring this new synthetic fibre. It became evident that a high degree of water-solubility, particularly that arising from the presence of a multiplicity of sulphonic or carboxylic groups, militated against any worthwhile affinity for cellulose acetate fibres. It was found that affinity was to be looked for among coloured compounds which were water-insoluble and which had a molecular size rather less than the conventional dyes for natural fibres, and that affinity increased in the presence of amino or substituted amino groups.

Suitable colouring matters were found amongst the simpler azo compounds and among some of the highly-coloured amino anthraquinone derivatives. Most of these had a ready solubility in solvents such as acetone and, indeed, the dyeing of cellulose acetate can be somewhat crudely considered as dissolving a coloured organic compound in cellulose acetate as an organic solvent. Such dyes, if water were to be used as the carrier medium, could only be applied as an insoluble suspension. It became a technological problem to produce these dyes in an extremely fine state of sub-division and to preserve the original small particle size from aggregation by the incorporation of suitable surface active agents and protective colloids. Finally, the dry powder so produced must disperse rapidly in an aqueous bath to give a uniform dispersion or suspension.

So highly have these physico-chemical techniques been developed that modern dyes of this class, the so-called dispersed dyes, give uniform suspensions which in some cases might well be mistaken by the casual observer for true solutions. In short, they have come near to the basic desideratum of the ease of application of the truly soluble dyes.

The dispersed dyes are, if anything, of enhanced importance today because of their usefulness in dyeing some of the modern synthetic fibres such as nylon and *Terylene*. The tight physical structure of these so-called hydrophobic fibres makes them difficult to dye. In other words, the underlying cause

of the desirable drip-dry properties of such fibres at the same time makes difficult the penetration of aqueous dye solutions and restricts the migration of dye molecules within the fibre.

The techniques applied for producing the dispersed dyes in a suitable physical form have had other far-reaching effects on the dyeing of synthetic fibres, in particular on the dyeing of viscose rayon. The production of a water-insoluble colouring matter or pigment within a fibre, giving a high standard of washing fastness, has been considered above. In the case of synthetic fibres which are made by forcing a solution or molten mass of polymer through fine holes in a spinnerette, it is a short step in reasoning to contemplate pigmenting or colouring the polymer mass before it is squeezed through the spinnerette. This technique is now practised on a considerable scale. The so-called 'mass colouration' of fibres requires extremely fine dispersions of pigment so as to obtain the maximum tinctorial effect and, also, to avoid any risk of blocking the extremely small holes of the modern spinnerette. This technique has become of importance in the modern colouration of viscose rayon. Its limitations are more commercial than technical; many fashion shades change from season to season and the problem of producing mass-coloured fibre without risk of obsolete stock is more difficult than if one manufactures white yarn or fabric and then dyes the appropriate shade according to demand at the time. Nevertheless, there are shades for which there is a permanent and regular demand—for example, black and navy blues, and here mass pigmentation scores. Thus, in this context, carbon black has now become an important modern 'dye'! A similar technique has found a small but useful decorative outlet in the mass-pigmentation of polyester threads with metallic powders, giving yarns a metallic lustre.

Vat Dyes

Physico-chemical methods of producing water-insoluble dyes in extremely small particle size and with ready dispersibility in water have also been applied to the vat dyes, mainly for the purpose of increasing the ease with which they can be 'vatted' to the leuco form for application to the fibre. Another modern device for simplifying the method of application for vat dyes is for the dye maker to convert the colourless leuco compound into its sulphuric ester which is readily water-soluble and therefore easily applied to cotton fabrics. When on the fibre these ester compounds, which are sold as such, can be reconverted to the original water-insoluble vat dye by oxidation on the fibre, losing the sulphuric ester water-soluble grouping in the process.

Metal-Containing Dyes

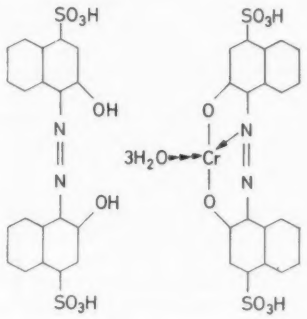
Another important modern group is that of the so-called metal-containing dyes. It was mentioned above that the early synthetic dyes had no direct affinity for cotton and had to be used by first impregnating the fibre or fabric with suitable metallic salts. These metallic salts or mordants had the ability to fix the dye on the fibre in the form of an insoluble metallic lake or salt. Madder or alizarine and other natural dyes had been fixed by similar techniques for centuries. It was later found that some of the synthetic dyes, even those which already had direct affinity for, say, wool or cotton, could be improved in washing fastness and in some cases in light fastness by after-treating the dyeings with solutions of appropriate metal salts such as those of chromium or copper. In general, chromium was found to be the most suitable metal for wool dyes whereas copper was more satisfactory with cotton dyes.

It is evident that such methods involving a two-step operation in which metal treatment and dyeing are two separate processes are at a disadvantage in both cost and convenience. There is a further disadvantage. When the metallic lake is formed the dye undergoes considerable change of shade, usually a deepening of shade—for example, from bluish-red to blue or from yellow to orange or brown. Such changes make precise colour matching of dyeings from batch to batch more difficult.

To overcome these disadvantages it became necessary to invent dyes with the metal already firmly fixed; that is, with the fastness properties and the change of shade already in-built and yet with enough direct affinity for the fibre to enable them to be dyed in a normal way from an aqueous bath. The achievement of this objective has been by no means simple, and the modern metal-containing dyes have indeed been evolving as a range during the last thirty years.

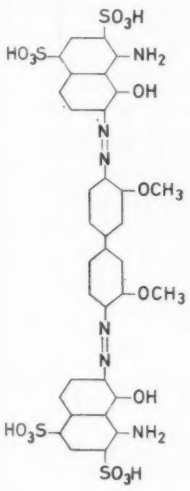
The most important members of the metal-containing dyes are those in which the chromophor, or colour-producing structure, is the azo link. It was found that by building certain molecular groups around the azo link to give a claw-like or 'chelate' structure capable of grappling to it a suitable metal atom, the whole dye molecule is given a greater strength and rigidity and the azo link given better protection against disintegration by light or oxidation. One of the commonest 'chelate' systems is the *ortho*dihydroxy azo structure—for example (*I*)—which is capable of co-ordinating or gripping firmly chromium as in (*II*). In certain cases *ortho*dimethoxy azo groupings can similarly be converted to co-ordination forms—for example, (*III*) can be converted by the dye maker into (*IV*).

Thus a blue dyestuff (*III*) discovered in the 1890s, which is too fugitive to light for many modern purposes, has now taken a new lease of life as form (*IV*) which has a very high fastness to light.

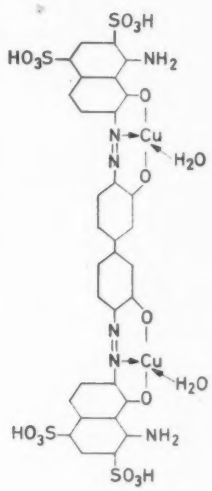


(*I*)

(*II*)



(*III*)



(*IV*)

Improvements in fastness of properties of dyes for wool dyeing has not only been achieved by the use of metal compounds. A very marked improvement in washing fastness of wool dyes was achieved with an invention in 1933 which was undoubtedly influenced by the emerging chemistry of synthetic detergents. It was found, particularly in azo dyes, that by introducing long fatty chains into the dye molecule at the same time as water-solubilizing groups such as sulphonic acid groups it was possible to strike an advantageous balance of properties, *i.e.* between the solubility required for easy dyeing and the dye's colloidal behaviour once within the fibre which made it more difficult to remove by water.

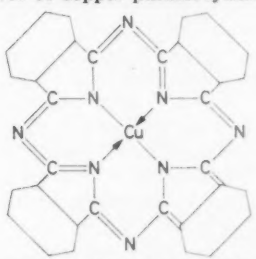
Phthalocyanine Dyes

It is not often that a completely new chromophor, or source of chemical colour, turns up. The discovery of copper phthalocyanine in the 1930s would, therefore, have been notable on this ground alone. The recognition of its structural family relationship with haemin the red pigment of blood enhanced its scientific interest. However, we are primarily concerned tonight with the importance of the phthalocyanines in modern dye technology. This importance derives not only from an attractive shade but in particular from outstanding fastness properties. The ability of copper phthalocyanine to sublime unchanged at 600°C, is evidence of its great chemical stability. The discovery by British chemists of copper phthalocyanine as an impurity in certain commercial manufactures of phthalimide, and the subsequent elucidation of its chemical structure by Linstead and co-workers, has often been recounted[1].

Copper phthalocyanine (*V*) is of course a water-insoluble pigment. It contains the copper atom firmly chelated within the claws of the outer organic structure. Great fastness to light is therefore to be expected. The purity of its blue shade, neither too red nor too green, makes it the blue component of choice for modern three-colour printing systems. It is the only modern pigment with fastness comparable to the metallic oxides and hence to find a permanent place on the modern artist's palette.

With its virtues of shade and fastness, it is not surprising that the dye chemist sought eagerly for ways and means of using the new chromophor for textile dyes. Copper phthalocyanine pigment in finely dispersed condition is indeed used in considerable quantity in the mass pigmentation of fibres to which we have already referred. The first water soluble derivatives of copper phthalocyanine to be

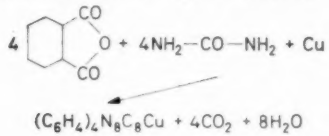
(*V*)



used for dyeing were disulphonic acid derivatives. These had a measure of affinity for textile fibres. and whilst they preserved a good deal of the high light fastness properties of the parent pigment, their washing fastness was of too low an order to give

them permanent importance. However, a considerable step forward was made in 1947 when HADDOCK and WOOD discovered that certain quarternary ammonium derivatives of copper phthalocyanine had water-solubility and affinity for cellulose fibres[2]. Most important of all, these derivatives readily regenerate a water-insoluble copper phthalocyanine within the fibre, thus preserving at one stroke ease of application and high fastness properties.

The most important technical process for the manufacture of copper phthalocyanine is that invented by Wyler after the constitution of the compound became known. The process consists in heating together phthalic anhydride, urea and a copper salt[1]. Having considered the complicated structure of copper phthalocyanine (*V*), let us write down the bare bones of Wyler's reaction:

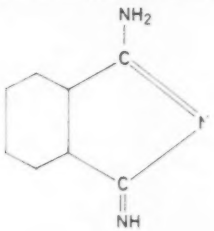


$$4\,C_6H_4(CO)_2O + 4NH_2{-}CO{-}NH_2 + Cu \longrightarrow (C_6H_4)_4N_8C_8Cu + 4CO_2 + 8H_2O$$

Copper Phthalocyanine

For sheer elegance and chemical imagination Wyler's invention, in my opinion, stands in the upper flights of organic chemistry. I remember a colleague of his and mine saying at the time with a twinkle in his eye, 'Dr Wyler, what a pity that you have to waste the four moles of carbon dioxide!'

The remarkable reactions by which phthalocyanines are formed have been of intense interest to organic chemists from the beginning. Much study has been made of the mechanism of the reaction, particularly with a view to isolating stable precursors or intermediates in the overall reaction. In 1956 the chemists of the Bayer Company showed that



(VI)

1–amino–3–imino*iso*indolenine (*VI*) is such a precursor compound[3]. It is stable enough to be marketed as such and is capable by appropriate treatment with a copper salt on the fibre of producing the parent copper phthalocyanine pigment within the fibre.

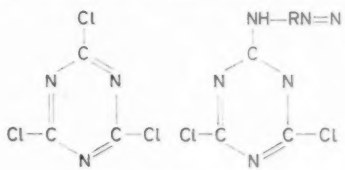
Procion Dyes

All the cases of modern dyes discussed here so far depend for their attachment to fibres on either (*a*) physical adsorption involving some measure of chemical affinity for the fibre, or (*b*) mere mechanical retention of insoluble particles of colouring matter within the fibre itself. A third method of attaching dye to fibre has always been the dye chemists' dream—namely, to do this by actual chemical reaction between dye and fibre. In such circumstances the dye would become chemically part of the fibre itself and it could be postulated with certainty that such a covalent link would give a substantial increase in the washing fastness of the coloured material. There have been several abortive attempts to solve this problem in the past, but it is only within the last four years that British chemists have produced a solution which is technically practicable and which has already become of major technical importance.

The first useful dyes of this kind are the *Procion* dyes, which are particularly suited to the dyeing of cotton or cellulosic fibres. The Procion dyes are freely water-soluble and can be applied to cellulose from a normal dyebath. Then, under very mildly alkaline conditions in the same bath, the dye reacts with the cellulose so that it is no longer either water-soluble or extractable from the fibre by a wide range of solvents. The generalized reaction can be written

$$S{\cdot}R{\cdot}X + HO{\cdot}\,Cell{\cdot\cdot} \longrightarrow S{\cdot}R{\cdot}O{\cdot}Cell{\cdot\cdot} + HX$$

where S is a water-solubilizing group, R is the colour structure and X is a reactive halogen atom.



(VII) *(VIII)*

For example cyanuric chloride (*VII*) has three reactive chlorine groups which can be made to react singly and in turn with, for example, amino compounds such as coloured amino azo compounds (*VIII*). If the amino azo residue in (*VIII*) contains a sulphonic acid group or groups it will indeed be a water soluble reactive dye, since the two remaining chlorine atoms in the cyanuric ring can react with cellulose under mildly alkaline conditions.

Dr VICKERSTAFF[4] has given in great detail the evidence for actual chemical reaction between the procion dyes and cellulose. There can be no doubt that they are extremely easy to apply; their fixation is very rapid and the finished dyeings have fastness

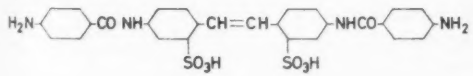
to washing comparable with that of many of the vat dyes. It is already clear that the underlying principle of reactive dyes has by no means been fully exploited. Indeed, within the last year a new range of dyes involving the reactive principle has been designed specifically for use on nylon. These represent a substantial step forward in the special problem of dyeing the more recent man-made fibres and especially of achieving high washing fastness.

Dyeing of the New Synthetic Fibres

Very little has been said here about the problems of dyeing polyamide, polyester and polyacrylonitrile fibres except to indicate that the physical structure which gives them many of their desirable textile qualities at the same time makes them more difficult to dye than the natural fibres. However, they can be satisfactorily dyed under commercial conditions although the dyer would undoubtedly welcome simplified methods of application and a greater versatility of available dyes. In this region the modern dye picture is by no means complete, but certainly chemists will in due time produce improved dyes either by further development of the concepts we have already discussed or by discovering yet new basic principles.

Fluorescent Dyes

In the early 1930s the author was much concerned with both experiment and speculation about the structural principles which confer substantivity or direct affinity for cotton, particularly molecular size and shape of substantive dyes. Partly to confirm certain theoretical conclusions compounds of the following kind were made[2]



(IX)

Compound (*IX*) is soluble in water, it is virtually colourless and 'dyes' cotton direct just like an ordinary direct dyestuff. Under ultra-violet light the colourless 'dyeings' had an intense blue fluorescence. Apart from a few minor uses the compound had at the time no great practical significance.

A few years later it was proposed to improve the whiteness of laundered fabrics by treating them not with the old-fashioned blue bag but with colourless compounds which had a blue fluorescence in the near ultra-violet. Compounds such as methyl umbelliferone were tried for this purpose but were found to be of limited practical value because they had virtually no affinity for cotton. It was then that these compounds became of technical and commercial importance. Since then many variations on the original structure have been made in order to produce various improvements in properties, such as freedom from yellowing on exposure to light, and also for the purposes of increasing the intensity of fluorescence. Fluorescent whitening agents have become an established feature in both laundry practice and detergent manufacture. It is therefore interesting to recall that these modern embodiments derive from an attempt to make some fundamental study of cotton affinity.

Selective Dyes

Space is not available to give a picture of the ingenious ways in which the dyer and the fabric designer use the modern dyes available to them, nor of modern high speed, continuous dyeing processes. Reference must be made, however, to one practical aspect of the selective affinity of a particular dye for a particular fibre. The fabric designer, either for economy or for a new aesthetic effect, may blend or weave together two or more different fibres. With a mixture of selective dyes of different colour the dyer can obtain a two- or three-shade effect from one dyebath. If the selective dyes are of the same colour, a uniform or 'solid' shade can be produced from one dyebath.

Conclusion

In conclusion, it is appropriate to recall that Sir William Pope along with others was deeply concerned during the First World War at the extent to which British industrial organic chemistry, and dye chemistry in particular, had fallen behind that of the Germans—to recall also his researches on the cyanine dyes designed to rectify the appalling weaknesses of our national situation on photographic sensitizers. The cause of all those British deficiencies was simply that we had not devoted enough money and effort to industrial organic chemical research. That situation has been radically altered since the First World War, although there is still no room for complacency. Nevertheless, Sir William would have taken pleasure in the fact that of five or six major discoveries made in the field of dyestuffs technology since the First World War, some four of these can be credited to British chemists—particularly the oustanding vat dye, Caledon Jade Green, the dispersed dyes for cellulose acetate, copper phthalocyanine, and the reactive dyes.

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[2] HADDOCK, N. H. *Research, Lond.* (1948) **1**, 687
[3] BAUMANN, F. *Angew. Chem.* (1956) **68**, 133
[4] VICKERSTAFF, J. *J. Soc. Dy. Col.* (1957) **73**, 237

ELECTRONIC MEASUREMENT OF PARTICLE SIZE

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A novel counter is described, which detects and sizes particles in suspension by means of their electrical resistance. This instrument can count red blood cells at rates exceeding 5000 particles per second, and with modifications is capable of determining the volumes of spheres as small as 0·2μ in diameter. The operation of the counter and its advantages over optical counters are discussed, along with its applications to biology, medicine, and industry.

IN RECENT years the need for automatic devices to count and size microscopic particles has become ever more apparent. The problem of particle size analysis is better known to industry than to science —it has been a hardy perennial in the coal industry and in the food industries, among many others. The increase in smog and other atmospheric contamination during the past decade in many places in the world has made the problem of nearly universal concern. During the last several years this concern has been extended to include radioactive fallout.

A variety of automatic optical counters, some capable of sizing, is produced commercially. Many of these have been designed specifically to count human red blood cells, which are particularly well adapted for optical instruments since their diameters, slightly less than 8 μ (0·008 mm), vary little and are well above the limit of resolution of the optical microscope. However in many dispersed systems the particles are irregular in size and shape, and often extend beyond the limit of optical resolution. There is no record of satisfactory performance of an optical counter applied to the counting and sizing of such particles. Even relatively large irregular particles present difficulties—counting becomes unreliable because indentations cause them to be counted more than once. Particle sizing is crude, at best, because the shapes of the particles are unknown; indeed, the very meaning of the term 'size' varies with the method used, depending on whether chord, perimeter, or cross section is measured.

These are fundamental difficulties for optical counters. While counting errors might be reduced by careful design, it is quite evident that sizing must remain a relatively unsolved problem. Furthermore, these difficulties increase enormously as particle diameters are reduced to sizes near and below the wavelength of light, in the neighbourhood of 0·5 microns. A new approach is required, and until recently there was no sign of one.

However, in 1956, W. H. COULTER[1] announced a novel counter for microscopic particles which detects particles by means of their resistance. Individual particles pass through an orifice containing an electrolyte, thereby changing the resistance of the contents of the orifice. Attempts at counting cells in suspension by measuring the resistance of the entire suspension had been made earlier by others, but this required a knowledge of additional factors, such as the distribution of cell sizes and their corresponding resistances—factors which were impossible to estimate at that time, and also which are variable during the course of growth of a bacterial culture. Recording the passage of single particles, on the other hand, is not thus limited, and the problem is reduced to one of simple enumeration.

Operation

The operational principle of a resistance counter is shown diagrammatically in *Figure 1*. Particles in suspension are aspirated through an orifice or aperture in the wall of a nonconducting tube, through which an electric current also passes. When a relatively nonconducting particle enters the counting aperture the resistance to electric current flow increases and remains larger until the particle leaves. The corresponding voltage pulse is amplified and counted electronically. The pulse amplitude distribution, which is related to the particle size distribution, can also be recorded electronically. Techniques of this kind are commonly used in nuclear physics—for example gamma-ray spectroscopy with a scintillation counter.

The change in resistance due to the passage of a particle may be calculated from simple physical principles. In the absence of a particle the resistance Ω between the electrodes depends primarily

upon the length L and cross sectional area A of the orifice, as well as the resistivity ρ_l of the electrolyte, according to the well-known relation,

$$\Omega = \rho_l L/A \qquad \ldots.(1)$$

When a small particle of large effective resistivity, $\rho \gg \rho_l$, enters the aperture, the resistance between the electrodes increases because the particle behaves like a nonconducting 'hole' displacing an equivalent volume of conducting solution. The altered resistance can be calculated by considering *Equation 1* to apply for the solution surrounding the particle. The particle itself is considered as a sum of incremental resistances in series, each of incremental thickness dl, and of cross section σ defined by the shape of the particle. The incremental resistance dR contributed by any segment of the particle is then given by

$$dR = \rho_l \, dl/(A - \sigma) \qquad \ldots.(2)$$

Integration of this expression is particularly simple when $a \ll A$, a being the maximum particle cross section. This applies to particles with diameters no greater than, say, 10 per cent that of the aperture: then a is no greater than 1 per cent of the aperture cross section. The result is

$$R = \Omega + \rho_l v/A^2 \qquad \ldots.(3)$$

where v is the volume of the particle. The corresponding change in resistance $\Delta\Omega = R - \Omega$ is

$$\Delta\Omega = \rho_l v/A^2 \qquad \ldots.(4)$$

Dividing each side of *Equation 4* by the corresponding side of *Equation 1*, and recognizing that the orifice volume V is given by $V = AL$, we find

$$\Delta\Omega/\Omega = v/V \qquad \ldots.(5)$$

This equation shows that for small particles of relatively low conductivity the change $\Delta\Omega$ in the resistance of the electrolyte in the orifice is directly proportional to the volume of the particle. Since the amplitude of the output pulse is directly proportional to $\Delta\Omega$, it follows that pulse amplitude is proportional to particle volume. This simple derivation implies that the measurement of small particle volumes is independent of particle shape. It must be pointed out that a more precise derivation, considering electric current flow and equipotential lines in greater detail, would show that pulse amplitude is not strictly independent of the shape of the particle. The proportionality would be retained, however, for particles of a common shape but different sizes.

As the ratio of particle cross section to aperture cross section increases beyond 10 per cent the proportionality between particle volume and pulse amplitude becomes an increasingly poorer approximation, with pulse amplitude accelerating rapidly. In addition, particle shape now becomes significant, even in this simple derivation, and more accurate expressions for the pulse amplitude are required. These are shown in *Figure 1* both for spheres and for right cylinders with axes aligned parallel to the direction of flow through the orifice, as a function of the parameter α. This parameter is the ratio of the maximum cross sectional area in the plane of the aperture to the area of the aperture itself, $\alpha = a/A$.

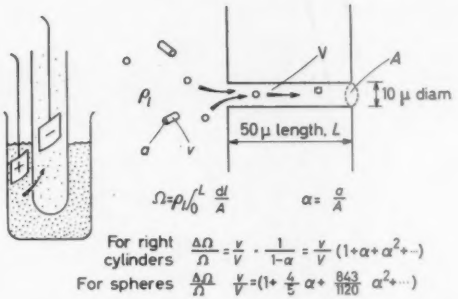

Figure 1. The counting orifice. The solution containing the particles is aspirated through a minute aperture through which an electric current also flows. See text for explanation of symbols

In principle, calibration of the orifice volume V and the resistivity ρ_l would allow this instrument to be used as an absolute device. However, small orifice volumes are difficult to measure because of the relatively large errors involved in determining the length and the diameter of a hole in glass with dimensions of about a thousandth of an inch. To date the resistance counter has been used only for analysis of relative particle sizes, with calibration of the aperture through the use of particles of known diameters if an absolute scale is required. The standard particles most commonly used for calibration are ragweed pollen, about 20 μ in diameter (varying somewhat with electrolyte and period of immersion), and the much more precisely calibrated polystyrene spheres* of about 1 μ in diameter, which have been commonly employed to calibrate electron micrographs.

Modification of the Coulter Counter

During 1956 the author was attempting to construct an optical counter for bacteria, when the Coulter Counter came to his attention. This instrument had been designed to count red blood cells at rates exceeding 5000 per second, an order of magnitude more rapid than most optical counters (see MORGAN[2] for example), when apertures about 100 μ in diameter

* Polystyrene particles with diameters from 0·088–1·171 μ can be obtained from the Physical Research Laboratory, Dow Chemical Company, Midland, Michigan.

Figure 2. The Coulter Counter (by courtesy of Coulter Electronics, Chicago, Illinois)

were used. In addition it was apparent that the complex optical equipment which must be continuously focused and refocused could be dispensed with; the Coulter Counter (*Figure 2*) does have a low power microscope, but its use is to ascertain that the aperture is open, not for viewing particles.

The theoretical advantages of a resistance counter were promising, implying as they did that bacteria and perhaps even smaller objects might be counted and sized. Since light is not used for detection, the lower limit for sizing is not determined, as it is for optical counters, by the wavelength of light. Furthermore it was easy to see that this method discriminates more successfully than optical counting against counts from unwanted particles: the aperture itself acts as a filter to exclude unduly large contaminant particles, which, if present, would overload the counting and sizing circuitry; discrimination against small contaminant particles is achieved by the increased resolution of the method, which follows from its sensitivity to particle volume rather than to particle cross section or diameter. Thus if background particles with ten-fold smaller diameters are present in the sample, they will contribute pulses with amplitudes reduced by a factor of 1000. But even more important, it seemed that this method might provide the distribution of particle volumes directly from the observed distribution of pulse amplitudes. This is not possible with an optical counter, since the cross section presented by the particle is a matter of chance, leading to a variable output-pulse amplitude for identical particles other than spheres, and requiring a statistical correction to give the true distribution. Except for a few simple cases, this correction is, in fact, impossible to establish with precision, since it depends upon the knowledge of particle shapes, and these are rarely known.

Preliminary trials using a Coulter Counter seemed to indicate that greater sensitivity was required: bacterial cells (*Escherichia coli*, about 2 μ in length and 0·5 μ in diameter) did give rise to an increase in counting rate, but the corresponding pulses were rather feeble, with amplitudes not greatly different from electrical noise pulses arising spontaneously in the amplifier. It was unlikely that a good test of the performance of the instrument could be carried out under these conditions—and a good test was necessary as the prospects of sizing with this instrument seemed dubious. The test of performance required both counting and sizing of particles as small as bacteria, and this in turn required the development of a method for constructing orifices some 10 μ in diameter. This was achieved by heating

and drawing out a heavy-walled capillary until the bore almost vanished. The tube was broken into segments, which were in turn ground and polished to discs about 0·001 in. (25 μ) thick.

It was immediately apparent that with a 10-μ aperture, bacteria could be counted. Pulse amplitudes were eight- to tenfold greater than the background noise. It became obvious, furthermore, that accurate sizing would require two additional modifications. In the first place the output pulse due to the passage of a particle through the aperture was round-topped, not rectangular as expected theoretically (the pulse amplitude should remain constant as long as the particle is contained within the orifice). To obtain rectangular pulses the electronic circuitry was modified, and in addition longer orifices—

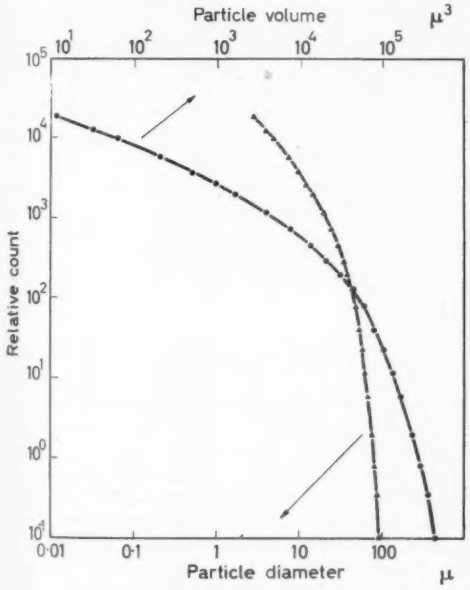

Figure 3. Integral size distributions of iron ore particles (by courtesy of Particle Data Laboratories, Inc., Elmhurst, Illinois). The circles indicate the relative counts for particles with volumes larger than the stated size, and the triangles indicate the same count for the corresponding diameters. Particles were dispersed in alcohol–Daxad dispersant and counted in 1 per cent NaCl solution with a 200-μ aperture

about 0·002 in.—were made, allowing the amplifier to reach full response to the presence of each particle before it left the orifice. The other modification was one permitting the collection of more accurate data by the use of direct measurement of the differential distribution of pulse amplitudes, a technique commonly employed with particle detectors for radioactivity. Normally, the Coulter Counter gives an integral size distribution as shown in *Figure 3*: a count includes all particles above a chosen size. The differential distribution, as in *Figure 4*, is of much greater interest, since it gives the number

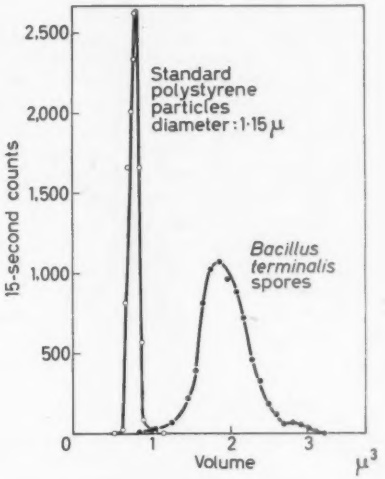

Figure 4. Differential volume distribution of Bacillus terminalis spores. The spores were counted in 1N HCl with a 10 μ aperture

of particles with their different volumes. It is often calculated from the integral distribution, but it may be obtained electronically with much more precision for the same counting time. If, in addition, data for both kinds of distributions are taken simultaneously, a continuous check of the reliability of the operation of the counter is provided by the running agreement between the two kinds of distributions. For these reasons a differential pulse-height analyser was added. The question now was 'Can bacteria and other small particles be counted and sized accurately?'

Counter Performance

The uniformly-sized polystyrene particles in the micron region made strict tests of the modified counter possible. In early tests[3] on comparing visual counts obtained with a haemocytometer to those with the counter, the latter was found to be an ideal instrument for determining concentrations of particles with diameters at least as large as 30 per

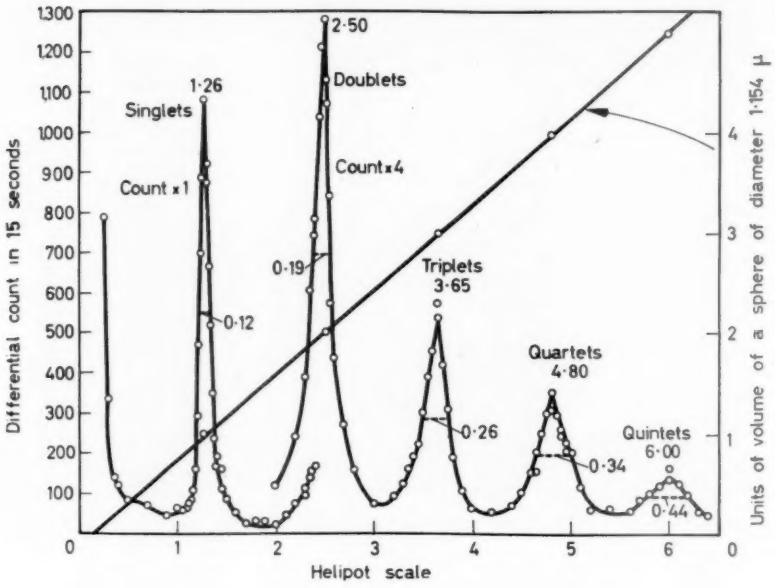

Figure 5. Calibration of counter performance in sizing aggregates of polystyrene particles 1·15 μ in diameter. The Helipot scale indicates relative pulse amplitude. The larger circles show the positions of the peak maxima for each aggregate. These are plotted against aggregate volume, in units of the volume of one polystyrene particle as shown for the ordinate at the right

cent that of the counting aperture. About three days was required to obtain data from haemocytometer counts with an accuracy approaching that obtained from the counter in about an hour. The accuracy of sizing was determined by comparing standard polystyrene particles of two different diameters. When one of these provided a calibration of the counter, the value for the other diameter obtained with the counter agreed to within 2 per cent of its known value. Furthermore, the resolution of the instrument was great enough to permit indentification of the presence of two groups of homogeneous particles differing in volume by as little as 0·05 μ^3. Since one μ^3 is 10^{-12} c.c., the corresponding mass sensitivity is finer than 10^{-13} g for biological objects, which ordinarily have densities near unity.

The modified counter is far more nearly linear in performance than was originally anticipated. This was demonstrated by allowing 1·15 μ polystyrene spheres to aggregate into groups of particles in hydrochloric acid suspension. These aggregates were then sized as if they were individual particles, giving the distribution shown in *Figure 5*: the peaks representing single particles, doublets, triplets, quartets, and quintets are uniformly spaced on the helipot (precision helically-wound potentiometer) scale, which is proportional to pulse amplitude. This uniformity is more clearly displayed by replotting the maximum of each peak against the known volume of the corresponding aggregate; the result is the straight line which is read on the ordinate scale at the right of the figure. The linearity of the points defining this straight line reflects the strikingly linear performance of the counter in responding to particle volume. (This line does not pass through zero because the fiducial point on the helipot scale was not matched with zero pulse amplitude as closely as might be desired; in fact, this is one method for accurately adjusting the zero position of the helipot scale.)

It must be made clear that the data of *Figure 5* may not provide evidence that the measurement of volume is independent of the shape of the aggregate, as would be the case were the particles certain to remain aggregated within the orifice. It is possible that aggregates disintegrate into individual spheres.

The volume flow rate of liquid through the orifice is rapid, reaching velocities as large as 3 m/s even with a 10 μ aperture. Shearing forces are created at the entrance to the orifice and within, which might be expected to overcome the relatively weak bonds between the aggregated spheres.

On the other hand, it is possible to estimate the magnitude of the effect of particle shape from the calculations of FRICKE[4] for prolate and oblate spheroids in suspension. A nonconducting prolate spheroid with axis of revolution four times as large as its diameter would give rise to a pulse with amplitude about 8 per cent greater than that for a sphere of equal volume. This corresponds to an overestimate of the diameter of the equivalent sphere of less than 3 per cent, a small correction, but one which would be observable with the precision available with this modified counter. The correction would be greater for oblate spheroids. These corrections cannot be calculated for particles of unknown shape or porosity; but one might obtain an estimate of roughness or porosity by sizing at several different values of resistivity of solution.

Thus these tests have shown not only that the resistance counter can count particles in suspension accurately, but that it is capable of sizing particles with unusual precision. They also show that the amplitude of the output pulse is proportional to particle volume for spherical particles with radii of about one-tenth that of the aperture, as predicted by *Equation 5*.

Applications in Biology and Medicine

The Coulter Counter has already been applied to the counting and sizing of a great variety of particles. Its most extensive use has been to count red blood cells, but it is also used to count the other elements of the blood, both leucocytes and platelets, and the many different kinds of cells from animal and human tissue cultures, normal and tumor strains. If these particles were spherical the corresponding range is about 2 μ for blood platelets to perhaps 40 μ for the larger cells in tissue culture.

The counter was used to make routine measurements of the size of the small cells such as bacteria and spores[3]. A typical differential volume distribution is shown in *Figure 4* for *Bacillus terminalis* spores, kindly made available by Prof. Philipp GERHARDT of the University of Michigan, Ann Arbor. This is not a true spore-volume distribution: the spores are surrounded by a large and filmy membrane, which add to the apparent volume of the spore. The small peak at the far right of the distribution is probably due to bacteria germinated from the spores during shipment: the magnitude of the peak agrees well with the estimate, about 1 per cent, from microscopic examination.

In the microbiological field the resistance counter allows the study of the dynamics of growth of cultures with a precision heretofore unattainable, and with convenience since counts may be made in the growth medium; for example it is now possible to study synchronously dividing cultures without the restricted statistical accuracy incurred by visual cell counts. Furthermore, the resolution available with the modified counter permits effects upon cell enlargement to be distinguished from those upon cell division at an early stage, say, after applying an antibiotic.

Recently, the modified counter has detected minute particles, as small as 0·2 μ in diameter, allowing some of the larger virus particles of feline pneumonitis to be counted automatically for the first time. These and other large viruses attacking animal cells, such as chicken pox and *Herpes zoster*, are not constant in size, but range from about 0·1–0·4 μ. The counter's sensitivity will have to be extended further before these viruses can be counted with confidence, and this would be most useful because present-day counting techniques are extremely laborious, involving electron microscopy and the counting of particles from photographs.

The listed range of the diameters of biological particles already counted is only some 200-fold, but the actual range is greater when inanimate particles are included; for example, *Figure 3* shows that iron ore particles greater than 90 μ have been counted. As with optical counters no upper limit is implied for the size of the particle which may be counted. In principle, the resistance method could be used, for example, for sizing muskrats or other animals.

Industrial Applications

Within the last two years the industrial applications of the Coulter Counter have become numerous and varied. It is valuable to industry because of its ability to size very small particles, the relative rapidity and simplicity of size analysis, and the ability to detect minute concentrations of particles. An estimate of the latter may be made from a knowledge of the sampling rate of the Coulter Counter: this rate is about 2 ml of solution per minute with a 100 μ aperture. Particles several microns in diameter or larger may be detected in smallest concentration, since for these there is no competing background due to electrical noise. Since counts of particles which are suspended at random in solution obey Poisson statistics it is necessary to count one hundred particles to achieve a standard error of 10 per cent in the estimate of concentration. This applies for a ten-minute

*Table 1. Samples for which particle size distributions have been obtained**

Abrasives
- Carborundum (silicon carbide)
- Diamond dust
- Silica
- Abr. powder (French pebbles)

Air Pollutants
- Fly ash
- Dust (air sample)

Atomic Energy Material
- Thorium oxide

Catalysts
- Fluid cracking (Davison)
- Fluid cracking (Filtrol)
- Silica alumina
- Clay (cheto)
- Carbon (activated)

Ceramics and Refractories
- Alumina
- Tungsten
- Glass frit
- Glass beads
- Magnesium hydroxide
- Magnesium oxide
- Zirconium oxide

Clay and Soils
- Clay (ball)
- Clay (inert)
- Clay (coatings)
- Clay (custer feldspar)
- Clay (ferric oxide)
- Kaolin

Cosmetics
- Face powder
- Hand lotion
- Permanent wave lotion
- Rouge
- Shampoo

Equipment Evaluations
- Paper pump machinery
- Dyestuff milling machinery
- Carborundum (dust collectors)
- Alumina grinding machines
- Filters (soil, charcoal and dust)

Explosives and Powdered Fuel
- Coke (coal)
- Coke (petroleum)
- Explosives
- Coal (powdered)

Filtering and Absorbing Media
- Carbon (activated)
- Dicalite

Food
- Essential oil (emulsion)
- Sugar (confectioners)
- Catsup
- Tomato paste
- Cocoa powder
- Milk powder
- Flour (wheat)
- Starch

Lubricants (Solid)

Metal Powders
- Tungsten
- Iron oxide
- Aluminum
- Silicon metal
- Zinc metal
- Tantalum metal
- Titanium metal
- Tantalum oxide
- Ferromagnetic
- Silver metal
- Silver oxide

Minerals
- Iron ore
- Mica powder
- Ore concentrate
- Gypsum

Miscellaneous
- Stearate (calcium)
- Stearate (lead)
- Stearate (zinc)

Paper Coatings
- Ink emulsions
- Wax emulsions

Paper fibres
- Classified pulps
- Beaten pulps
- Refining process

Petroleum and Fuels
- Lubricating oil contaminants
- Rolling mill oil
- Hydraulic oil contaminants

Pharmaceuticals
- Carotene (B)
- Mineral oil and water emulsion
- Radiographic agent
- Insulin

Phosphors
- Zinc sulphide
- Calcium phosphate

Photographic Materials
- Xerox powder
- Toner

Pigments and Fillers
- Carbon black
- Calcium carbonate
- Barium sulphate (sludge)
- Barium sulphate (sparmite)
- Lead chromate (chrome yellow)
- Mica powder
- Titanium dioxide
- Zinc oxide
- Red lead
- Lead peroxide
- Vat yellow and vat olive

Polymers—Lattices
- Polyvinyl acetate latex
- Vinyl siloxane
- Resin emulsion
- Polyvinyl chloride (geon)

Portland Cement

Seed Crystals
- Alumina hydrate

Standard Reference Materials
- Arizona dust
- Glass beads
- Pollens (mono-sized)
- Polystyrene spheres (mono-sized)

Textiles
- Cellulose
- Wool

Water and Sewage Solids
- Raw water
- Settler concentrates

* By permission of Coulter Industrial Sales Co., Elmhurst, Illinois

count where the concentration is five particles per ml, and even lower concentrations may be estimated. These concentrations are several orders of magnitude lower than that required in light scattering methods, which are limited by the intrinsic light scattering of the pure solution.

Such exceptional sensitivity makes the resistance counter extremely useful for establishing standards of purity in the preparation of particle-free products. An example is in the petroleum industry, where particles in suspension in fuels and lubricants are of increasing concern because of their effects upon high speed engines in aircraft and rockets. Tests of these materials require compatible polar nonaqueous solvents with conductivity provided by an appropriate salt, for example for diesel oil, acetone and potassium thiocyanate. Particle concentration is also of concern in the testing of town's water supplies, and in the measurement of air pollution in industrial areas. In the latter case, of course, filter devices have been found adequate for determining the mass of pollutant and a resistance counter offers special advantage only in the analysis of particle size.

The rapidity and accuracy of particle sizing confers upon resistance counting a great advantage in industrial applications. Analyses which previously

would have required days using electron microscopy or sedimentation techniques now can be performed within an hour. In industry this facilitates process control in the production of materials for which no previous test was economically feasible, so that the products could only be tested after manufacture. This applies particularly to the production of cement, explosives and powdered fuels, foods, pharmaceuticals, photographic materials, and pigments. Products which have been analysed with the resistance counter are indicated in *Table 1*.

The Coulter Counter has consequently been used to evaluate or select machinery upon the basis of performance. For example the counter was used to select the most satisfactory of a series of grinders for reducing the solid lubricant molybdenum sulphide to particles of preferred size.

One of the greatest advantages of resistance counting for industrial purposes is the extended range of the method, permitting accurate sizing of smaller particles than was possible with previous optical counters.

Further Potentialities

A description of the capabilities of the Coulter Counter requires some consideration of its potentialities. Predictions of this kind, of course, are always coloured by the point of view of the author. The most probable uses of the counter are rather obvious extensions of present applications of the instrument. Some are extensions of the method to virgin fields.

In cytology, for example, such cell components as nuclei and mitochondria of human cells are now within the range of the counter. Since studies of enzymatic reactions have already been performed with nuclei of graded sizes, it is only a matter of time before this technique is wedded to the counter. In medicine, studies of red and white blood cell sizes, rather than simple counts alone, may well extend our knowledge of blood pathology, and will facilitate early detection of some diseases.

A virgin field is marine biology, where the organisms of interest are already suspended in an electrolyte. Plankton counts should be readily obtainable —knowledge of oceanic distribution should allow the prediction of many biological events. More than this, it is possible in principle at least to determine the number of vastly larger creatures of the sea, up to good-sized fish, although in this case it would involve driving them through a rather unwieldy aperture. The method appears more promising for determining the changes in fish populations in lakes and ponds, using channels as apertures. For example in salmon runs, the number of fish, their sizes, and their total bulk could be obtained. Counting alone would be as simple as determining human traffic with photocell detectors; and it would be subject to the same kinds of errors if fish, too, are gregarious. The method could present a distinct advantage over photocell counting at night or in murky waters.

This may seem unduly imaginative; however, it should be noted that another remote field of application is contemplated, that of snow archaeology. MARSHALL[5] has employed the counter in a study of particulates layered in polar ice. He believes it may be possible to obtain an annual record of atmospheric particulate fallout reaching back 2000 years from core samples of snow and ice taken in Antarctica (personal communication).

The resistance technique should also aid the physical sciences, for example in the study of factors involved in solid–liquid interactions, and for investigating cavitation and bubble formation, and turbulent flow in both large and small orifices. It is obvious that the study of colloidal phenomena will benefit greatly if the range of detection can be extended below 0·1 μ.

This list is incomplete in that applications to other fields, agriculture and geology, for example, have been neglected, Indeed, it could not be complete, since the broader capabilities of any device are made apparent only by the development of associated arts and sciences. Would Prof. Hans GEIGER have suspected that his device might become technologically indispensible?

It is a truism that continued advance both in science and in industry requires constant development of new and improved techniques of measurement, as well as the invention of the new instruments required for such purposes. These improvements and devices allow the critical testing of theories and also, through increases in accuracy, often result in uncovering new and unsuspected phenomena. The Coulter Counter, yet in its infancy, may well be such an instrument.

The author's work discussed in this paper was performed under the auspices of the U.S. Atomic Energy Commsision. Thanks are due to Mr Robert Berg of Coulter Industrial Sales Co., for providing examples for the section on Industrial Applications, and for technical advice and criticism.

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NEW WAYS WITH INORGANIC POLYMERS

J. H. S. GREEN

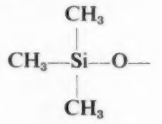
There is an increasing need for polymeric materials combining the flexibility, elasticity and solubility of organic polymers with the high thermal stability of inorganic materials. An account is given of recent work of ANDRIANOV whereby organic groups are joined to purely inorganic skeletal chains. Polymers have been prepared based on the silica structure –Si–O– and the corundum structure –O–Al–O–Al–, whilst others contain elements such as titanium, tin, boron, and phosphorus linked through chains to silicon and oxygen. New important uses of the materials are described.

THE rapid growth of polymer science is resulting in the continual discovery of materials with new and even quite unexpected properties and one aspect of this development is the attempt to improve upon important physical properties of the polymeric structures. It has long been known that such materials based on a backbone of carbon–carbon bonds are beset almost inevitably with certain limitations, perhaps the most serious of which are their susceptibility to oxidation and their low thermal stability. For example, although polystyrene is used in the electrical, radio and other industries, its low softening temperature (80°C) and mechanical strength have been disadvantages. Now, the thermal properties have been improved by modifying the structure by introducing substituents such as one or more methyl groups into the benzene ring, or, more markedly, by the introduction of fluorine atoms into the vinyl group. Thus, the polymer derived from $C_6H_5—CF=CF_2$ combines valuable properties of styrene and *Teflon*, having a softening point of 240°C and low dielectric loss.

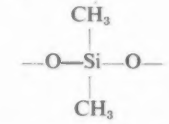
But at the same time there is a rapidly increasing need for materials combining the flexibility, elasticity and solubility of organic polymers with the very considerable thermal stability of various naturally occurring inorganic macromolecules which also contain chains of atoms. At first sight a wide gap seems to exist between the organic chains and such substances as the silicates, quartz and corundum. However, recent work has gone some way towards narrowing this gap by the preparation of materials with inorganic back bone chains to which organic groups are attached. The preparation of such materials derived originally from organic compounds of silicon, and firstly these will be briefly considered.

The Silicones: General Considerations

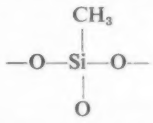
During the last twenty years there has been a rapid growth of the industry of the silicone polymers and their widespread application[1]. These substances are obtained, for example, by the acid hydrolysis of alkyl (or aryl) substituted halogenosilanes—R_2SiX_2, where R is CH_3 or C_6H_5 and X is Cl, for example—and various types of structure can occur in the products. It is convenient to distinguish three such fundamental groups which can be exemplified, where R is CH_3, by



(*I*) *Trimethylsiloxy or monofunctional* (*M*) *group*



(*II*) *Dimethylsiloxy or difunctional* (*D*) *group*



(*III*) *Monomethylsiloxy or trifunctional* (*T*) *group*

In all cases the distinctive properties of the silicones are related to the silicon–carbon (Si—C) and silicon–oxygen (Si—O) bonds occurring in all cases.

The silicones were found to be resistant to moisture, relatively chemically inert, stable to oxidation and the action of sunlight, oxygen and ozone. All these properties derive from the high stability of the Si—O bond, and from the greater resistance of the Si—C bond to oxidation than the carbon–carbon bonds in organic polymers. Further, the polar Si—O bond protects the Si—C bond from reaction with oxygen. An important factor in the increased thermal stability and resistance to oxidation of silicones is the difference between the ageing processes for the latter and for organic polymers[2]. With an organic polymer two independent processes are involved: (*i*) cross-linking, resulting in loss of elasticity and increase of hardness and brittleness, and (*ii*) degradation or breaking of chain links and consequent decrease of molecular weight.

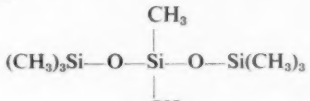
At high temperatures this degradation occurs chiefly at the ends of the chains and results in loss of low molecular weight volatile products, but it continues until the polymer is substantially broken

down. In silicones, on the other hand, it has been suggested that the Si—O bonds are unaffected and initial fission is of the weaker Si—C bonds leading to volatile organic oxidation products. In this case the polymer is not broken down; instead, at the position of each broken Si—C link a new S—O bond is formed so that cross-linking and increase of the branched structure and of molecular weight occurs. The thermal stability is therefore dependent on the nature of the organic group, and the following order of decreasing thermal stability has been established[3]:

$$C_6H_5 > CH_2{=}CH_2 > CH_3 > C_2H_5$$

These considerations apply to silicone polymers with a two or three-dimensional structure; those with a linear structure are less resistant to degradation, and fission of both the Si—C and Si—O bonds occurs. (On the other hand, recent work[4] suggests that with polydimethylsiloxane oil, the C—H and Si—C bonds are not broken since the products of breakdown all have the elementary composition $(CH_3)_2SiO$.)

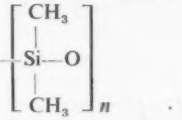
Silicones have found very important uses as lubricants and, with thickeners such as lithium stearate, as greases for use for example in ball bearings at elevated temperatures. Such applications arise from the small change of viscosity with temperature; thus the change for liquid silicones is some fifty times less than for petroleum greases, whilst at the same time the coefficient of compressibility is found to be much higher. These properties are connected with the relatively weak interactions between the polymer chains; also, with increase of temperature, the coiled molecular chain opens out, increases in length and thus increases the viscosity. It follows that such effects might be dependent on the size and nature of the organic groups linked to the carbon atoms, and this is found to be the case[5]. For example, the activation energy for viscous flow increases sharply when the two central methyl groups in



Hexamethyl—2—dimethyltrisiloxane

are replaced by an ethyl and a chlorophenyl group. A similar increase takes place if the number of chlorine atoms in the phenyl group is increased.

Investigation of the relaxation of dielectric loss with temperature shows that the maximum for this loss lies at about −100°C. This illustrates a further important property of these materials, namely that the advantageous physical properties persist over a wide range of temperatures; in general silicones show little susceptibility to low temperatures. In the case of polydimethylsiloxanes,



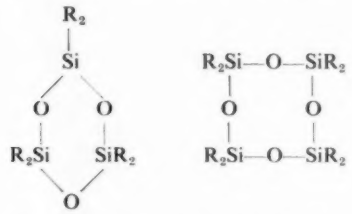
the second-order transition temperature is at −90°C, and certain marked differences are found from natural rubber[6]. Thus crystallization in the silicone elastomer proceeds rapidly, and the latter does not change at low temperatures whilst rubber does. These differences again are due to differences in structure between the Si—O—Si chain and that in organic polymers. These silicone rubbers, therefore, exhibit a high thermal resistance (up to 250°C), whilst they retain a constant elasticity over a wide temperature range. Materials of molecular weight in the range 600,000–900,000 can withstand temperatures down to −65°C and this lower limit can be reduced still further, to −90°C giving, for example, improved frost resistance, by the introduction of a small proportion of phenyl groups in place of the methyl groups[7].

Other applications of the heat resistant organosilicon compounds which have been reported[8] include reinforced plastics and use as lubricants, liquids for hydraulic systems, heat transfer media, anti-foaming additives and pump oil; they are also used as coatings possessing good adhesive, impregnating, water repellent and heat resisting properties. Of great potential value is the expectation[8] that linear polymers with fibre forming properties may be found by the synthesis of chains containing hydrocarbon, ester, *iso*cyanate or other similar groups *in addition* to siloxane groups.

Polyorganosiloxanes

In the above discussion, examples have been mentioned of silicon polymers in which organic groups are attached to silicon atoms linked together by alternate oxygen atoms, as in D groups. The basic structure is that of silicon dioxide-silica, and the silicates, and it has been pointed out that since certain Si—C linkages are very stable, the combination provides good thermal stability compared with organic polymers. Such compounds can be formed from organo-silanediols by a process of intermolecular condensation, *e.g.*

and it is of interest that such a reaction was observed (for R = C_6H_5) by Kipping in his pioneer researches. Depending on the size of the organic group R, heat or a catalyst may be required for the reaction to occur. The larger size of the silicon atom and the greater valence angle of oxygen allow the formation of much larger rings than in carbon compounds, and cyclic structures are also formed in the reaction, such as



with up to eighteen or more members. These cyclic products have an unfavourable effect on the properties and methods have been developed for their conversion into linear structures.

Table 1. Part of the periodic table

	III	IV	V	VI
1st short	B	C	N	O
2nd short	Al	Si	P	S
1st long		Ti Ge	V As	Se
2nd long		Zr Sn	Sb	
3rd long		Pb	Bi	

Hydroxy or alkoxy (—OCOR) end-groups in the organosilicon polymers are highly reactive. In the case of the methyl silicone oil obtained from the hydrolysis of dimethyldichlorosilane, the non-volatile portion contains high molecular weight compounds of the type

$$HO[Si(CH_3)_2O]_xSi(CH_3)_2OH$$

where x is a large number. (That is to say, it contains chains of D units terminated by OH groups.) To render this material more stable it is desirable to replace these end-groups by non-reactive groups giving structures such as

$$(CH_3)_3SiO[(CH_3)_2SiO]_xSi(CH_3)_3$$

On the other hand, use can be made of the reactive end-groups in two different ways. The first of these is in reaction of the organosilicon polymer with alkyl resins, themselves containing a large number of hydroxyl groups, or with epoxide resins, thereby obtaining new materials of valuable properties. Silicones with a large number of hydroxyl groups also show an improved compatibility with hydrophilic resins such as the important phenol-aldehyde and melamine-aldehyde resins. A second use of the reactivity of these hydroxyl groups, however, leads to new compounds of great significance[9].

Inorganic Polymers and the Periodic Table

The potential formation of covalent bonds is an obvious first consideration in inorganic polymers. *Table 1* shows a part of the periodic table listing

Table 2. Some patent and other claims for uses of inorganic polymers[10]

Polymer	*Use claimed*	*Reference*
Low molecular phosphonitrilic chlorides	Flame-proofing agent for textiles.	U.S.P.2,596,935 B.P. 700,822.
Polymeric titanium carboxylates OOCR | TiO | OOCR (R = $C_{17}H_{35}$ *etc.*)	Surface active agents; water repellents; rust inhibitors.	U.S.P. 2,484,508; 2,621,194; 2,621,195; 2,621,196; 2,708,203 J. STEPANEK, *Prakt. Chem.* (1955) **3**, 31
Polymers from organic derivatives of *ortho*titanic acid	Drying oil accelerators; snubbing layer for binding of gelatin to photographic film; modifiers for resin polymers.	U.S.P.2,620,318; 2,676,102 B.P. 728,751
Copolymers of organotitanium and organosilicon compounds	Curing agents for resins; water repellents for textiles; photographic snubbing layers.	B.P. 728,751

elements in groups III to VI which are known to form such bonds. Various polymers derived from these elements have been described[10], and some of the rather miscellaneous but widespread uses which have been claimed for these polymers are shown in *Table 2*.

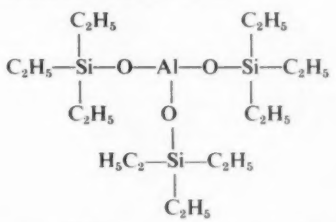
A more systematic approach to the use of elements other than carbon and silicon to form the backbone chains of polymers is provided by the recent work of K. A. ANDRIANOV and co-workers; the use for this purpose of aluminium, titanium, boron, magnesium and other elements has been established[2,5,11]. The general aim is to attach to the inorganic chains alkyl-, aryl-, or alkyl-(aryl-) groups of the structure ($R_3Si—O$) as what are termed 'framing groups'. Just as the polyorganosiloxanes simulate the structure of silica and quartz, so these newly developed compounds utilize the strength and stability of other naturally occurring, purely inorganic materials, such as corundum (Al_2O_3), aluminium silicates, boron and titanium silicates, polytitanates, and so on. At the same time, the introduction of the organic groups surrounding the inorganic chain confers wholly new properties including flexibility and solubility, which are characteristic of organic polymers.

Polyorganometallosiloxanes

The first approach to such substances was the above mentioned reactivity of hydroxyl groups in polyorganosiloxanes. For example, reaction of triethylhydroxysilane with aluminium, in the presence of mercuric chloride as a catalyst, gave 88 per cent yield of nonaethylaluminoxytrisiloxane:

$$6(C_2H_5)_3SiOH + Al \longrightarrow [(C_2H_5)_3SiO]_3Al + 3H_2$$

If this structure is written out as



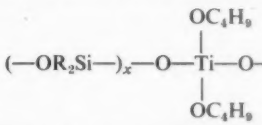
we see that the skeleton structure —Si—O—Al— has been created; the product is crystalline, melting at 159°C. Other reactions were then developed for obtaining the same fundamental structure with various organic groups attached. For example, the simultaneous alkaline hydrolysis of dimethyldichlorosilane ($(CH_3)_2SiCl_2$), phenyltrichlorosilane ($C_6H_5SiCl_3$) and aluminium chloride gave polyaluminoxytetra - (dimethylphenyl - disiloxane), a polymer in which aluminium was linked to silicon through oxygen, with organic groups attached. A very important property of such polymers is that, though brittle solid substances, they are soluble in organic solvents such as benzene, alcohol and acetone, whilst evaporation of such solutions gives a thin transparent, heat resistant film.

The stability of such compounds was found to be high. So far as acid hydrolysis was concerned, they were not inferior to natural aluminosilicates such as kaolin, as can be seen from *Table 3*.

Table 3. Percentage destruction of Si—O—Al bonds in: I, polyaluminoxytetra-(dimethylphenyldisiloxane); II, nonaethylaluminoxytrisiloxane; and kaolin[2]

Time	*I*			*II*			*Kaolin*		
Hours	Percentage HCl at 96°C								
	10	20	30	10	20	30	10	20	30
1	54	60	67	79	87	93	91	88	100
5	65	69	—	91	98	—	100	100	—
10	70	72	72	91	99	100	—	—	—
22	79	—	—	—	—	—	—	—	—

Successful attempts were next made to prepare polymers in which the molecular chains contained silicon, titanium and oxygen atoms. These were obtained by the hydrolysis of mixtures of organosilicon compounds, such as alkyl (or aryl) chlorosilanes, and the butyl esters of *ortho*titanic acid (*cf. Table 2.*) In this there were structures such as



were obtained. The creation of polymers containing other elements linked through chains to silicon and oxygen has been achieved with tin, boron—the polymers are viscous, light brown liquids, but again are soluble in organic solvents—antimony, phosphorus and lead, by the use of various reactions which need not be detailed here.

The next development was the preparation of polymers based on chains not containing silicon. Thus a chain formed only of aluminium and oxygen, —O—Al—O—Al— would be similar to that in corundum. Such compounds were first reported by ANDRIANOV in 1957 and were obtained from the substance nonaethylaluminoxytrisiloxane mentioned above. Hydrolysis of this by water or by blowing in wet air at 20°C resulted in a steady increase of the viscosity of the solution. In the initial stages, the

reaction yields mostly cyclic or linear unbranched soluble polymers. At a certain stage, however, depending on the amount of water used, branched, and three dimensional network structures are formed; these are insoluble and the solution therefore gels. At higher temperatures the rate of polymerization is slower but still depends on the amount of water present. The reaction is attended by a change of the initial crystalline product into a material which did not crystallize on cooling, and by the formation of hexaethyldisiloxane and triethylsilanol as by-products. These facts could be explained by a mechanism of stepwise condensation, where for simplicity we write R for C_2H_5:

$$(R_3SiO)_3Al + H_2O \longrightarrow (R_3SiO)_2AlOH + R_3SiOH$$

$$2(R_3SiO)_2AlOH \longrightarrow (R_3SiO)_2AlOAl(OSiR_3)_2 + H_2O$$

$$(R_3SiO)_2AlO\left[\begin{array}{c}-Al-O-\\ |\\ OSiR_3\end{array}\right]_x Al(OSiR_3)_2$$

The resulting polymer has a molecular weight of 4100 which corresponds to a degree of polymerization of 23; in general these polyorganosilylaluminoxanes are transparent colourless or brownish, vitreous substances, and are soluble in benzene, alcohol and acetone. Evaporation of such solutions applied to surfaces gives heat resistant films.

It is known that titanium can replace silicon in some silicates[12] and therefore it might be expected that titanium compounds analogous to these aluminium polymers could be prepared. This is found to be the case. Dodecamethyltitanoxytetrasiloxane $[(CH_3)_3SiO]_4Ti$ was found to hydrolyse in the presence of acid catalysts to form polymers of various molecular weights but all of the composition (R=CH_3):

$$(R_3SiO)_3Ti-[O-Ti-]_xOTi(OSiR_3)_3$$
$$\quad\quad\quad

MINIATURE A.C. SERVOMOTORS AND SYNCHROS

C. ROBSON

Engineering Department, Smiths Aircraft Instruments Ltd

The extended use of servomechanisms and automatic controls in aircraft and guided weapons has led to the development of a range of miniature synchros and servomotors. Brief descriptions of the types and constructions of these instruments are given, together with an indication of the advances made since 1945. This is the third article in the *Microinstruments* series.

DURING the second world war closed loop control systems were used extensively for such military purposes as gunfire control systems on land, sea and air. This led to a demand for motors and position and rate measuring instruments specially designed for servomechanism application. At the end of the war more accurate instruments and controls for aircraft were needed. On the larger aircraft there were difficulties due to the increasing distance between transmitting instruments and their associated indicator instruments mounted on the pilot's instrument panel. Aircraft instrument designers, therefore, began to use small electric servo-mechanisms and torque synchros to a greater extent[1,2].

During the last ten years the reliability of airborne electrical power supplies and instruments has been well proven. Advantage has been taken of the great flexibility afforded by electrical circuitry and instrumentation to produce navigational systems and automatic pilots which accept data regarding airspeed, height, direction *etc.* from sensing elements, and, after processing the data, present flight information and instructions either to the pilot *via* his instrument panel, or direct to the aircraft controls. Such systems, which are generally a.c., depend to a large extent upon the use of a.c. synchros and servomotors. A large modern transport aircraft would use at least thirty-five synchros and perhaps twenty servomotors.

Because of the tendency to reduce the volume and weight of all aircraft equipment, development work on servomotors and synchros over the past ten years has been mainly devoted to miniaturization with better performance and accuracy; at the same time materials and design have been improved in order to prolong service and storage life under increasingly severe environmental conditions. In common with other aircraft equipment, modern synchros and servomotors are required to perform reliably over an ambient temperature ranging from $-65°C$ to $+70°C$ and under severe conditions of vibration[3]. With the advance of guided missile engineering, an even greater need for miniaturization, combined with more rigorous operating conditions, has arisen.

In both the United Kingdom and the United States a range of small precision a.c. synchros and a.c. servomotors with frame sizes from $\frac{1}{2}$ in. to $3\frac{3}{4}$ in. in diameter now exists. The outline dimensions of the various frame sizes conform to internationally agreed standards, and efforts are being made to standardize performance figures for each frame size. The development of this range began in the U.S.A. in 1946, when the U.S. Navy Bureau of Ordnance sponsored an instrument component development programme—indeed, the international frame sizes are commonly known as *BUORD* frame sizes. Similar work was initiated by the British Ministry of Supply later. The standard frame sizes are designated by numbers which refer to the maximum diameter of the cylindrical housing in tenths of an inch. If this is not an exact number of tenths the next highest tenth is used; for example, the maximum outside diameter of a size 11 frame is 1·062 in. and that of a size 08 frame is 0·75 in.

a.c. Synchros

The word ' synchro ' was originally peculiar to the U.S. Navy Department and has now been adopted generally for a class of electromechanical devices used for data transmission. These are used commonly in conjunction with one or more similar devices to derive a visual indication of, (or electrical signal dependent on), the relative displacement of the shafts or bodies to which they are attached, or to develop a torque tending to reduce such displacement to a minimum[4]. Synchros can be obtained for either a.c. or d.c. operation, but the a.c. synchro is in more common use especially in aircraft servomechanisms.

The a.c. synchro consists of a rotor mounted in bearings so as to rotate inside a stator. Both stator and rotor are laminated and carry two pole windings. The stator is slotted and wound in a similar manner to that of a polyphase induction motor stator and usually has two or three windings, whereas the rotor may be a salient pole type or a slotted drum type with one, two or three windings. In one type of

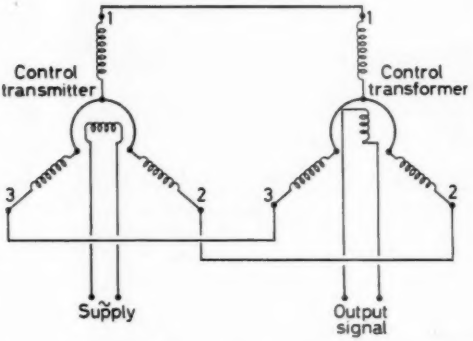


Figure 1. Connection scheme for a pair of control synchros

synchro the rotor carries no winding but is energized *via* an airgap by means of an additional stator winding in order to reduce rotor mass and bearing friction. Normally, the rotor is supplied electrically by brushes and sliprings, or by ligament wires when full angular rotor freedom is not required.

Most synchros are contained in standard housings but one type, called a slab synchro, comprises rotor and stator laminations, windings and leads only; the diameter is large relative to the axial length and its main use is in gymbal assemblies. Another construction is that of the rotatable stator synchro, which is in effect the standard cased synchro mounted in additional bearings in a fixed shell frame. Extra sliprings are added for the outer winding supply and a drive gear for the rotating outer element.

Synchro Types

Only a brief outline of the description and uses of the various types of a.c. synchro is given here but more detailed accounts have been published elsewhere[1,2,5,6,7].

There are three main groups of a.c. synchros: resolver elements, control elements and torque elements. These groups are derived from the different applications of the synchro rather than any difference in construction. In fact, the same synchro in certain instances may be used either as a torque or a control element, although in general a particular synchro is designed to give optimum performance for only one mode of operation.

Resolver Synchros

The resolver synchro is a synchro which is capable of resolving an electrical vector into two perpendicular components or of compounding, in conjunction with a servomechanism, two perpendicular vectors into a resultant vector. The stator and rotor of the resolver synchro are similarly wound, each with two windings whose axes are mutually perpendicular. If a winding on one member is supplied with a.c. at a constant voltage, the a.c. voltage induced in the two windings of the other member are proportional in magnitude to the sine and cosine respectively of the angle of the rotor relative to the stator, (a change of sign is denoted by a 180° phase shift of the output voltage).

The resolver synchro is frequently used as a phase shifting transformer, when the two windings of either stator or rotor are fed from a two-phase a.c. source. In this case the voltages on both secondary windings are constant in magnitude but correspond in electrical time phase angle to the rotor angle with, of course, a constant 90° phase difference between the voltages of the two output windings.

Control Synchros

Control synchros may be further sub-divided into three types: control transmitters (CX), control transformers (CT) and control differential transmitters (CDX).

The control transmitter carries a single primary winding on its rotor and three identical stator windings, with equispaced axes, which are connected together at one end to form a star point, the other ends being taken to the synchro terminals. The rotor winding is connected through sliprings and collector

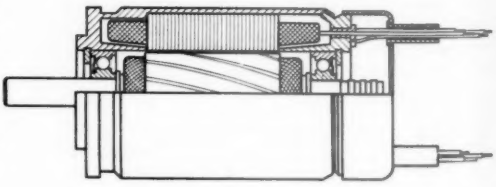


Figure 2. Drawing of a modern synchro sectioned to show the through bore construction

brushes to the synchro terminals. It is usual to employ a salient pole construction for the rotor of the control transmitter.

The control transformer has the same system of windings as the control transmitter but the rotor is invariably of the slotted drum type, with its winding distributed over a number of slots. It is energized by its stator windings from another synchro. *Figure 1* shows a general scheme for the connection of a control transmitter–control transformer pair; the corresponding stator terminals of both synchros are connected together and the primary rotor winding of the transmitter is supplied with a.c. Voltages of the same time phase but differing in magnitude are induced in the three transmitter stator windings and cause proportional currents to flow in the control transformer stator windings. The resultant alternating magnetic flux produced in the control transformer takes up an angular position corresponding to that of the transmitter rotor winding axis. Thus, the output voltage obtained from the control transformer rotor winding is proportional to the sine of the difference of the angular positions of the two rotors. This output voltage may be used, after amplification, to control a servomotor.

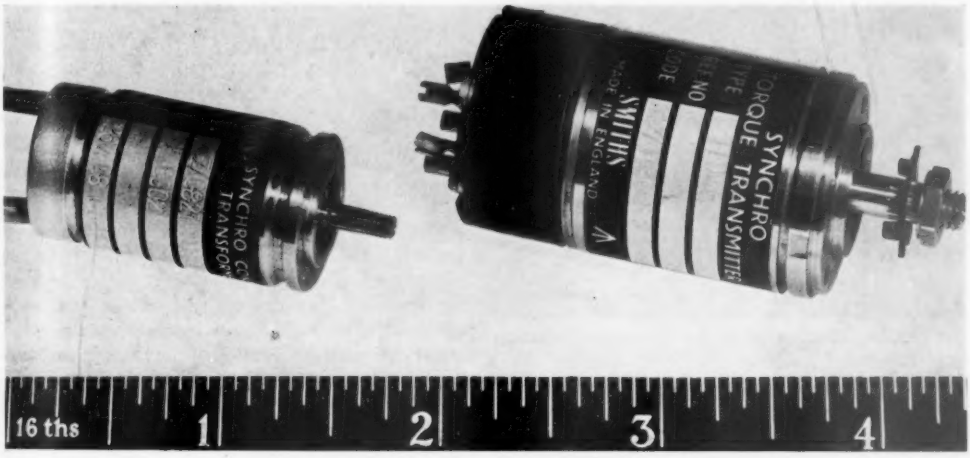


Figure 3. Size 08 and size 11 synchros

The control differential transmitter (CDX) has three stator windings similar to the other control synchros, but the slotted drum rotor also carries three equispaced windings, star-connected. With its stator windings connected to the control transmitter stator and its rotor windings connected to the control transformer stator, it modifies the action of the synchro control chain so that the control transformer output voltage is proportional to sin $(\theta_{CX} - \theta_{CT} \pm \theta_{CDX})$ where θ_{CX}, θ_{CT} and θ_{CDX} are the rotor angles of the control transmitter, the control transformer and the control differential transmitter respectively. The sign of the θ_{CDX} term is dependent upon the sequence of the differential transmitter connections.

Torque Synchros

If, in *Figure 1*, the supply voltage were connected to both transmitter and transformer rotor windings in parallel, the two rotors would pull into angular alignment. If one were turned the other would follow although any torque load on the follower shaft would produce a misalignment. In this case the synchros are being used as a torque transmitter (TX) and a torque receiver (TR). A torque differential synchro is also available. This is connected into the system in the same way as the control differential and the three synchro shafts behave rather like a mechanical differential gear. If the shafts of two of the synchros are turned and then held, the shaft of the third synchro will align at an angle which is the sum or difference (depending on the sequence of the connections) of the other two rotor angles. The accuracy of the system depends upon the torque loading of the output shaft and the system is normally used to drive light loads, such as a pointer.

Synchro Design

It will be seen that the synchro action depends on the change in mutual inductance between the stator and rotor windings, when the rotor is turned. To ensure accuracy the variation in mutual inductance must be precisely related to the angular movement of the rotor. This can only be achieved by the symmetrical arrangement of the magnetic and electrical circuits. Care must be taken during manufacture that the airgap is uniform, that the rotor axis is central in the stator bore, that the laminations are accurate and accurately assembled and that the windings are made to precise limits.

The size of the miniature synchro limits the number of slots that can be used in its design so that particular attention must be paid to the elimination of 'slot ripple' in the airgap magnetic flux. This means that the number of slots in the rotor and stator must be carefully selected, the slots on at least one member must be skewed and in some cases the winding distribution in the slots must be specially arranged.

Perfect symmetry can never be consistently obtained, due to manufacturing tolerances, but the design can be executed in such a manner as to minimize the effect that the manufacturing tolerances have on the accuracy of the synchro. An example of this is the 'through bore' construction which originated in the U.S.A. and is very commonly used in both synchros and servomotors. This is illustrated in *Figure 2*. The machine is designed so that the finished bore diameter of the stator laminations is exactly equal to that required to house the ball bearings. The front end of the stator housing is formed to provide a support for the front bearing, and the rear bearing is supported by the rear end cover plate. The stator pack is wound, inserted into the housing, together with the rear end cover plate, and the whole assembly is locked together by spinning the rear end of the stator housing over the rear end cover plate to form a lip. After impregnation, a parallel bore is then machined through the assembly to match the ball bearing outside diameter. The rotor, complete with bearings, can thereafter be assembled into the stator and located by snap clips fitted into retaining grooves in the stator housing bore. The assembly is completed by the fitting of the brush gear and cover. This method has largely eliminated the build up of those tolerances which result in eccentric mounting of the rotor in the stator bore and has improved accuracy and reduced working airgap lengths.

In order to meet the rigorous environmental demands of modern aircraft, materials such as nickel iron for laminations and corrosion-resistant steel for housings, shafts and ball bearings are now used

Figure 4. Drag cup servomotor before final assembly

in miniature synchros. Windings are encapsulated in epoxy type resins to provide better insulation resistance under conditions of severe humidity.

dom in 1945 with those of modern synchros. For ease of comparison, the relevant information is listed in tabular form (*Tables 1* and *2*).

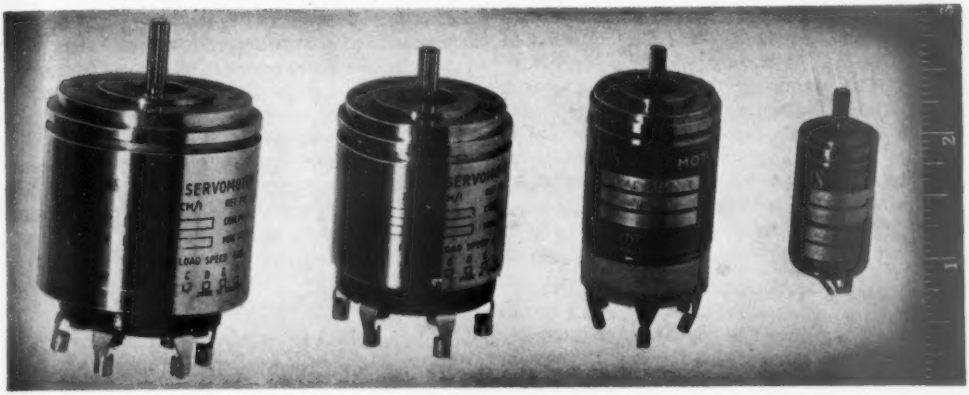


Figure 5. Size 07, size 11, size 15 and size 18 servomotors

An indication of the advances made in the design of the miniature synchro over the past fifteen years can be gained by comparing the dimensions and performance of synchros made in the United King-

Table 1. Control synchros: a = 1945 2 in. synchro; b = 1945 3 in. synchro; c = Modern size 11; d = Modern size 08

	a	*b*	*c*	*d*
Outside diameter, in.	2·5	3·375	1·1	0·8
Length, in.	4·5	5·5	1·75	1·375
Weight, oz.	32	64	4·25	1·75
Rotor moment of inertia, g/cm²	170	950	2·5	1·4
Electrical accuracy, (minutes of arc)	±15	±9	±7	±10

Table 2. Torque synchros: a = 1945 2 in. synchro; b = 1945 3 in. synchro and c = Modern size 11

	a	*b*	*c*
Outside diameter, in.	2 5	3·375	1·1
Length, in.	4·5	5·5	1·75
Weight, oz.	32	64	4·5
Rotor moment of inertia, g/cm²	170	950	2·5
Following accuracy with pointer load, degrees	±1	±0·5	±1

Figure 3 shows some examples of modern synchros in international frame sizes.

a.c. Servomotors

The majority of instrument servomotors used in airborne applications are a.c. and of the induction motor type, although hysteresis motors[8] have sometimes been used. The induction motors may have either a squirrel cage rotor or a 'drag cup' rotor.

The Drag Cup Motor

The drag cup motor has been defined as an induction motor, the rotor of which consists of a cup of conducting material inside which is a stationary magnetic core. The idea of this design is that by removing the magnetic material from the rotating structure to the fixed inner core, rotor mass, and consequently moment of inertia, is kept low. The absence of separate rotor bars gives smooth starting free from the 'cogging' action that can occur due to slot ripple in the airgap magnetic flux of the squirrel cage motor. Unfortunately this design demands a relatively large airgap length which limits the torque available for any particular frame size. A photograph of a drag cup servomotor is shown in *Figure 4*. The rotor is mounted in jewelled bearings and the construction is inverted so that the wound stator is mounted inside the drag cup and the cylindrical laminated magnetic return path is built into the outer casing.

The Hysteresis Motor

The hysteresis motor is an a.c. motor with a stator similar to that of the induction motor but with a rotor consisting of a tube of unmagnetized permanent magnet material. Space does not permit a more detailed description here, but futher information may be obtained from some of the references supplied[8,9]. The torque of the hysteresis motor is approximately constant over its entire speed range and the motor will run in synchronism. This characteristic is undesirable for most positional servomechanism use but it can be of advantage for use with rate servomechanisms.

The Squirrel Cage Motor

The squirrel cage induction motor is well known. As designed for servomechanism use, it normally employs a high resistance rotor winding in order to provide a torque which is approximately inversely proportional to rotor speed. The stator is wound two phase. One, the reference phase, is usually continuously excited. The other, the control phase, is supplied from an amplifier to give the necessary proportional and reversing control. The design is aimed at maximum stall torque/inertia ratio and smooth starting with low control phase voltages.

Servomotor Design

High stall torques are obtained with minimum length of airgap and the limiting factors are manufacturing dimensional tolerances. Here again, the through-bore constructional technique has been used to achieve airgaps of the order of 0·001–0·002 in. destroys smooth starting and running with low control phase voltages.

Stator and rotor laminations are made from nickel iron to prevent corrosion and for the same reason the stator housing, rotor spindle and ball bearings are made from corrosion-resistant materials. The stator windings are normally resin encapsulated to give good insulation resistance under extreme humidity conditions.

The present range of servomotors built into international synchro frame sizes is quite extensive and sizes ranging from 05 up to 31 are available. *Table 3* shows a comparison of performance figures between small servomotors available in 1945 and modern miniature servomotors in the international frame size range. Representative examples of modern miniature servomotors are shown in *Figure 5*.

Servomotor Combinations

Certain systems have, from time to time, demanded special forms of servomotor with additional devices built into the motor frame. These special servomotors have become available for general use. In all cases, the moment of inertia is increased by the addition of the device but this penalty is often outweighed by the extra advantages offered to the servomechanism designer. Some of the devices which can be obtained are listed below :

(1) The Drag Cup Generator

The drag cup tacho-generator provides a rate signal which may be used for stabilization or integration

Table 3

	Outside diameter in.	*Length* in.	*Weight* oz.	*Rotor moment of inertia* g/cm²	*Torque* g/cm	*No load speed* rev/min	*Frequency* c/sec.
1945 2 in. motor	2·5	4	32	150	320	2800	50
1945 3 in. motor	3·375	5	80	1500	850	2800	50
Modern Size 07	0·7	1·2	1·25	0·18	8	9000	400
Modern Size 11	1·1	1·375	4·5	1·1	62	2500	50
	1·1	1·5	4·5	1·1	40	6200	400
Modern Size 18	1·8	2	12·25	4·0	250	3400	60
	1·8	2	12·25	4·0	150	4800	400

The rotor moment of inertia is kept to a low figure by making the rotor diameter as small as possible. As the maximum practicable number of winding slots is limited in a miniature servomotor, extreme care has to be taken by the designer in the selection of the rotor–stator slot ratio and of the slot skew angles in order to minimize magnetic cogging which

purposes. It is similar in construction to the two phase drag cup motor. One winding is supplied with a.c., the other winding provides a voltage of supply frequency which is proportional to the rotational speed of the drag cup rotor. When the direction of rotation reverses, the phase of the output voltage shifts through 180°.

(2) *The d.c. Eddy Current Brake*

This normally takes the form of a drag cup rotor rotating in the magnetic field of a stator. The stator winding is supplied with d.c. current. The resultant brake action modifies the damping of the servomotor. The d.c. supply voltage can be controlled to provide variations in the servomechanism damping factor for various modes of operation. This method consumes part of the power output of the servomechanism. For this reason the tachogenerator method of stabilization is favoured by most servomechanism designers—especially with the larger servomotor sizes.

(3) *The Permanent Magnet Eddy Current Brake*

This device is similar to that outlined in *2* above, but the d.c. winding is replaced by a permanent magnet. The magnet strength can be varied within limits during manufacture to provide the necessary damping for a particular application. At least one design exists where screw adjustment of the effective magnet strength is provided for individual setting in the particular servomechanism.

(4) *Inertial Damping*

If the permanent magnet of the eddy current damping device described in *3* above is mounted in bearings instead of being fixed in the motor frame, the resultant damping action on the servomotor is modified. When the motor accelerates or decelerates the usual eddy current braking torque is set up between the magnet and the drag cup. As the magnet is free to rotate, however, it tends to follow the drag cup rotation but more slowly due to its greater inertia. Maximum damping occurs during maximum motor acceleration or deceleration and the damping is negligible at steady speeds so that the no load speed of the inertial damped servomotor is almost the same as that of the equivalent standard servomotor.

(5) *Integral Gearheads*

Electric servomotors are invariably coupled to the driven load through reduction gears and packaged gearheads specially designed to match the standard international frame size servomotors are now available. The gearheads conform to standard servomotor dimensions in diameter of mounting spigot and output shaft and a range of fixed gear ratios are obtainable for each frame size. Backlash is kept to a minimum and the gearheads may be bolted to a standard servomotor to form an integral motor–gearbox construction of uniform diameter. Two gearheads can be mounted in cascade, if required, to give ratios higher than the standard range.

Future Development

Development trends in miniature servomotors and synchros over the past few years have been towards smaller frame sizes such as 08, 07 and 05 but the practical size limit has almost been reached with the size 05 units which are now becoming available. The present phase of development is in the direction of higher operating temperature. Claims have already been made by U.S.A. manufacturers for synchros that will withstand 200°C with a future target of 400°C.

For some time past, in both the United States and this country, manufacturers of servomotors and synchros have become extremely price conscious and great attention is being given to design and manufacturing methods in order to reduce manufacturing costs. Cost reduction will be further encouraged by the growing demand for these components, due to the increasing use of automatic controls and computers, not only in the aircraft and guided weapons field but in the whole of industry.

The author wishes to express his thanks to the management of Smiths Aircraft Instruments Ltd for permission to publish this article, and for the photographs contained in it.

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A RUSSIAN MACHINE TRANSLATION DICTIONARY

H. S. H. MASSEY

The difference between the Russian machine translation dictionary and an ordinary dictionary is discussed, a distinction being drawn between grammatical and lexical information about a word. It is pointed out that words receive relative, and often 'zero', values in translation, examples being given. The problem of polysemia is treated and examples of a programme to deal with it are given.

A FAIRLY recent article in the Russian journal *Voprosy Yazykoznaniya* [Linguistic Questions][1] throws an interesting light on a Russian approach to the problem of compiling a dictionary for machine translation (MT). The principles upon which the work is based appear to be a combination of the syntactical and semantic analysis approach of the Massachusetts Institute of Technology and the polysemia approach of the Rand Development Corporation. What is more, it would seem that at least a partial solution of the problem of polysemia in a context where the meaning is only clear from an extended text[2] can be achieved by the MT dictionary described.

The Russian MT dictionary differs from an ordinary one in several ways. Firstly it is divided into separate units corresponding to the languages to be treated. Each word in the source-language dictionary is given the number of its equivalent in the target-language dictionary; for translation in the other direction the words in the target-language dictionary are allotted indices showing the numbers of their equivalents in the source-language dictionary. Secondly, the dictionary of each language is divided into a section of monosemantic words and a section of polysemantic words, the monosemantic word section being further subdivided into groups of terms belonging to particular spheres of science (*e.g.* mathematics, physics) and a group of widely used monosemantic words. This type of structure, it is said, ensures accurate and speedy translation and enables the expansion of individual sections of the dictionary without disturbing its general structure. The section of polysemantic words, which is an experiment in the complete formalization of the semantic analysis of polysemantic words, is a new departure from a linguistic point of view.

The third peculiarity of the dictionary is that it contains not only a list of lexical units (words) but also a definite set of grammatical characteristics for each word, which is not fully formalized in ordinary dictionaries. The MT dictionary's systematized grammatical description of each word has been called the 'invariant characteristics of the word'. The fourth property of the dictionary is that it provides a system of relative word values, relating the lexical system of the target-language to that of the source-language. This is closely related to the fifth property, namely that the dictionary provides 'zero values' for words, *i.e.* those cases when a word should not be translated as a separate lexical unit.

Grammatical Information

The author distinguishes lexical information about a word from grammatical information by considering everything which occurs according to a rule to be grammatical and everything that is an inherent property of the word to be lexical. For the human translator it is sufficient to have these two forms of information in a separate dictionary and grammar, but the two must be combined in a MT dictionary. Any word may have two kinds of grammatical category inherent in it: the grammatical category determining the way a word changes whilst still preserving the same value independent of the use of that word in a sentence, and that which determines the change in value of a word according to the surrounding sentence. The first category is used to establish a system of invariant (or dictionary) word signs, whilst the second is used to establish a system of variant (or contextual) word signs.

Taking Russian nouns as an example, the variant signs are number and case and the invariant signs are the type of declension, the type of root, the gender, whether it is animate or inanimate, whether it is appellative or not, the degree to which it acts as a pronoun, its peculiarities in formation and the lexical group to which it belongs. For the Russian adjective the invariant signs are the type of root, its category of pronominality, its peculiarity in formation and the lexical group to which it belongs; the variant signs are the gender, number, case, degree of comparison, *etc.* The dominating sign in a

word's system of grammatical signs is that for the part of speech, which is one of the invariant signs.

The systems of invariant and variant signs are naturally different for different languages, but in the dictionary only those important for MT are taken into consideration. Many of the grammatical characteristics of traditional grammars do not appear in the dictionary, whereas there are many specially compiled ones that do. The system of invariant signs in the MT dictionary contains all the initial data necessary for subsequent grammatical analysis of a word in a sentence.

Lexical Values

The last two of the dictionary's properties are brought about by the specific character of the lexical values of the words as fixed in the MT dictionary. All translators realise that they cannot limit themselves to those meanings of a word found in a dictionary but have to amplify them in the light of the context they have before them. A bilingual dictionary, therefore, should not fix a system of values for the words of any language but a translation of this system into the target-language. In order to achieve this the author has introduced the concepts of the innate and the relative values of words.

The innate value of a word is taken to be that value the word has within the framework of the language to which it belongs; the relative value is that value (or that system of values) which the word acquires when it is translated into another language. These two values do not always coincide. For example, the English adjective ' good ' in combination with the noun ' chance ' acquires a relative value, when translated into Russian, containing the quantitative characteristic of the word ' shansy ', whilst the English reflects a qualitative characteristic: ' to have a good chance ' is ' imet' mnogo shansov [to have many chances] ' (and not ' khoroshiye shansy [good chances] '). To take another example, the word ' amount ' can be rendered into Russian, depending on the context, as ' summa [sum] ', ' itog [total] ', ' kolichestvo [quantity] ', ' ob'em [volume] ', *etc.* None of these is a value ' for the occasion ' or a particular nuance of some other value, but a definite value of the word confirmed by constant use. The lack of relative values in a MT dictionary can almost make nonsense of the dictionary's work, and therefore the necessary amplifying must be done in advance and fixed in the dictionary.

A particular case of the relative value is the ' zero value ', *i.e.* that case when a word should not be translated into the target-language as a separate lexical unit. For example, when translating the phrase ' it is interesting to note ' into Russian only the two words ' interesno otmetit' [interesting (to) note] ' are needed, and the three words ' it ', ' is ' and ' to ' have a zero value. The rôle of such words boils down to a modification of the value of the word or words to which it is attached in a sentence; therefore they are given invariant signs in the MT dictionary in the same way as other words. Auxiliary words are the usual ones to have zero values but even semantically independent words may have them, *e.g.* ' make ' = ' delat' ', ' make + sure ' = ' ubedit'sya + O ', ' make + ready ' = ' prigotovit' + O ', and so on. In the case of idiomatic expressions which are equivalent to only one word in the target-language all the words except the ' key-word ' are given a zero value.

Polysemia

It is the author's opinion that an idioms dictionary can be included in the section of polysemantic words, the idiomatic usage of a word being reflected in the general system of indications which provide for the correct translation of words which cannot be translated monosemantically into the target-language.

The author considers that the problem of polysemia can be solved satisfactorily for all languages if the following two methods are used:

(*1*) *Division of the MT dictionary into a series of ' special dictionaries '*—corresponding to the various spheres of human activity (mathematics, physics, *etc.*, *etc.*). The polysemia of words within such a dictionary is considerably reduced. A standard English–Russian dictionary, for example, gives ten different renderings for ' high ', but the mathematical dictionary reduces this to three: ' vysokiy [high] ', ' bol'shoy [great] ' and ' vysshego poryadka [of a higher order] '. In Chinese, Japanese and other languages the polysemia of words is no less considerably decreased.

(*2*) *Contextual analysis of the word*—If we take polysemia to be the ability of a word to appear in more than one type of context we can make rules for that ability by establishing typical contexts. Determination of typical contexts is achieved by statistical classification of the possible contexts of a word. The following programmes have been worked out by the Institute of Precision Mechanics and Computing for the contextual analyses of two English words. (The following system of linear notation is used: 1st number (or letter)—number of instruction; number (or letter) in brackets: 1st—number of instruction which should be transferred to if the check receives a positive answer, 2nd—if there is a negative answer.)

AVAILABLE

171 (a, 172):	Check the word being analysed for ' available '
a (I, b):	Check the first word to the right for ' commercially ' (*)[a]
b (II, c):	Check the first four words to the right for the combination ' at + the + starting + point '
c (III, IV):	Check the first noun to the left for the sign ' name of instrument ' or for the group ' method, theorem, formula . . .'
I (o):	Translation: ' imeyushchiysya [available] ' (adjective) Translation of word found: ' v prodazhe [on sale] ' (adverbial phrase)
II (o):	Translation: ' zadannyy [set] ' (adjective)
III (o):	Translation: ' primenimyy [applicable] ' (adjective)
IV (o):	Translation: ' dostupnyy [available for use] ' (adjective)

AFTER

56 (a, 57):	Check the word to be analysed for ' after ' and the absence of the sign ' adverb '[b]
a (I, b):	Check the next word to the right (**) for a noun with the sign ' subject '[c]
b (I, c):	Check the next word to the right (**) for a noun followed by a verb with the sign ' predicate ' or with the indices of a predicate[d]
c (II, d):	Check the preceding word for ' one ' and the following word for ' another '
d (III, e):	Check the nearest preceding verb to the left for belonging to the group ' pattern . . .'
e (IV, V):	Check the next word to the right (**) for nouns of the group ' method, rule . . . '
I (o):	Translation: ' posle, togo kak [after] ' (conjunction)
II (o):	Translation: ' za [behind] ' (preposition governing the instrumental case)
III (o):	Translation: ' s [from] ' (preposition governing the genitive case)
IV (o):	Translation: ' po [according to] ' (preposition governing the dative case)
V (o):	Translation: ' posle [after] ' (preposition governing the genitive case)

Notes on the programme:

[a] The indices * and ** indicate a necessity to apply rules for missing out independent words.

[b] A word may receive this sign in the *Homonyms analysis* programme.

[c] Some place names in particular may receive this sign in the dictionary.

[d] A single description is given to the formal index of the predicate.

In view of the claims of the author it would be interesting to see how the proposed dictionary would deal with the problem set by BAR-HILLEL[2] of translating ' The box was in the pen ' taken from the paragraph ' Little John was looking for his toy box. Finally he found it. The box was in the pen. John was very happy.'

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1960 ESSAY COMPETITION FOR SCHOOLS

THE *Research* Essay Competition for Schools was instituted in 1957 with the purpose of encouraging scientifically-minded school pupils to write clearly and comprehensibly about their work; thus it was hoped to assist in raising the standard of the writing of scientific reports in the future.

The 1960 competition has reverted to its original form. Schoolboys and schoolgirls are asked to write a report of 1000 to 1500 words on any recent piece of practical work or special project they have carried out in chemistry, physics or biology. The author of the best report, in the opinion of the judges, will receive a prize of books to the value of £15 and there will be a second prize of books to the value of £10. In addition, books to the value of £15 and £10 will be awarded to the school libraries of the first and second prize winners respectively.

Full details of this competition are available from the publishers of *Research*, 4 and 5 Bell Yard, London, W.C.2.

PROCESSING BY IRRADIATION

1. Sterilization of Medical and Pharmaceutical Products

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This article discusses the lethal action of ionizing radiations on micro-organisms and describes the application of this effect to the sterilization of pharmaceutical and medical products.

THE recent opening of a large Co^{60} gamma irradiation plant at Wantage (*Figure 1*) focuses attention on the progress made in this country in the technological development of ionizing radiation as a method of sterilization. This plant will be made available to British Industry and also to hospitals for the sterilization of large quantities of material for clinical and marketing trials. Ionizing radiation is already used commercially in America by Ethicon Inc. for sterilizing catgut sutures and in this country by several firms for such articles as arterial prostheses and catheters. Near Melbourne, Australia, a plant of 150,000 curies is in use for the sterilization of goat hair used for carpet manufacture, and other animal fibres. A further 350,000 curies are on order for the extension of the Australian plant.

Radiation is not the answer to all sterilization problems, but its advantages for many products over other methods are becoming apparent now that practical experience is accumulating. Although a slight rise in temperature may occur if very high dose rates are used, such as can be achieved with electron accelerators, radiation sterilization is essentially a cold process. This means it is possible to sterilize heat-sensitive articles on a production line basis rather than a batch basis as is necessary with ethylene oxide, the only other practical cold-sterilizing agent. One may also use a wider range of packaging materials, including the heat-sensitive plastics, than is possible with conventional techniques.

There are two types of ionizing radiation now in use, gamma radiation and high-energy electrons from a machine. The two differ chiefly in the power of penetration. Gamma radiation is the more penetrating and may be used to process articles which are up to two feet thick. The penetrating power of electrons is dependent upon the energy to which they are accelerated, but even irradiation with 3 MeV electrons from both sides will not allow articles of more than about an inch thick to be sterilized. The current unit of dose for both gamma rays and electrons is the rad which is an arbitrary unit corresponding to the absorption of 100 ergs per gram of material irradiated. The original unit of radiation was the roentgen (r) and it is still used widely in the medical profession. It is defined by the amount of ionization produced in air but suffers from the practical disadvantage that the energy deposited varies according to the material irradiated. Whereas one roentgen deposits about 83 ergs per gram in air, the same quantitiy of radiation deposits about 93 ergs per gram in biological tissue. This latter dose is called the roentgen equivalent physical (rep). Both the roentgen and the rep have now been largely superseded by the rad*.

It is as well to state categorically that irradiation with Co^{60} gamma rays or electrons of similar energies cannot induce radioactivity in the material irradiated.

Microbiological Aspects

An important feature of the lethal effect of radiation on bacteria is that death is not immediate, unlike the effect of heat for example. Many functions such as respiration and motility may continue for several hours after irradiation, and during this period various treatments may affect the viability of the cells. This is of some importance when sterility tests are performed on irradiated materials since the composition of the medium which is used may affect the number of survivors detected. A recent investigation showed that blood agar was one of the best media for making plate counts of irradiated organisms[1].

* In this article where doses are quoted from other reports, roentgens have been converted to rads by multiplying by 83/100 and reps by multiplying by 93/100

Figure 1. A general view of the package irradiation plant at Wantage showing in the foreground storage racks which hold the packages before they are automatically conveyed into the irradiation chamber. (*Crown copyright reserved*)

If the logarithm of the number of survivors of a radiation treatment is plotted on a graph against the dose of radiation, the result is frequently a straight line. Sometimes a flatter portion is found at the beginning of the curve; this occurs with *Clostridium sporogenes* (*Figure 2*). Bacteria do, of course, have different sensitivities to radiation and *Table 1* gives data which enable a comparison to be made between different species. Many pathogenic organisms are among the more radiosensitive, including the causative agents of tubercolosis, puerperal fever, boils, 'blue-pus' and typhoid. Spores are generally more resistant than the vegetative forms of bacteria and are the main consideration when calculating sterilizing doses. The most resistant organism so far described is the non-sporing *Micrococcus radiodurans*[2], which is a red-pigmented heat-sensitive coccus isolated from meat products in America. It is non-pathogenic and has not so far been reported in the British Isles.

Theoretical Sterilizing Dose

As we have seen, the inactivation of bacteria by radiation is frequently an exponential process, and this means that there is no such thing as a 'lethal dose' which is just sufficient to kill every organism. As the dose increases the number of survivors decreases although theoretically it never becomes zero (in this respect radiation is analogous to heat). The sterilizing dose will depend on the estimated initial degree of contamination and the final level of survival which can be tolerated. When the initial viable count is divided by the final viable count, the resulting figure represents the overall degree of reduction of the bacterial population and may be called the *inactivation factor*. For heat processed foods, inactivation factors of 10^8 to 10^{14} are common because of the danger of *Clostridium botulinum*, and radiation doses have been calculated which will produce this standard[3,4].

For medical products and pharmaceuticals it is difficult to estimate the inactivation factors normally achieved by heat processing. It is customary to use as a test organism the most resistant one likely to be encountered and *Bacillus stearothermophilus* is often used for this purpose in heat processing. It can be calculated from survival curves[5] that heating one strain of this organism at 120°C for twenty minutes (which is the standard of the U.S. Pharmacopeia) results in an inactivation factor of only 5×10^2. In practice such resistant strains are seldom encountered and very much higher inactivation factors are usually achieved. In the following estimation for radiation sterilization, we have assumed

that an inactivation factor of 10^7 is desirable for a test organism; *Clostridium sporogenes* has been chosen as being representative of the most radiation-resistant group of bacteria likely to be encountered. (Some, but not all, strains of *Bacillus subtilis* have a resistance comparable to that of *Clostridium sporogenes*). The survival curve in *Figure 2* extends over six log cycles. If it is extrapolated a further log cycle to give an inactivation factor of 10^7, the dose required is 2·4 Mrad*. HILL and PHILLIPS[6] recorded the radiation inactivation of *Bacillus subtilis* in freeze-dried penicillin and from their data one can estimate that an inactivation factor of 10^7 would need a dose of 1·5 Mrad. Their strain of *Bacillus subtilis* does not appear to be particularly resistant however.

It should be made quite clear that the organisms and survival curves chosen for the above estimations are only examples of the way in which the sterilizing dose may be calculated. Experience at Wantage has so far shown that 2·5 Mrad is an adequate sterilizing dose for every organism tested but this may be modified as more data become available. There is still a real need, however, for more information about the survival of such organisms as *Clostridium welchii* and *Clostridium tetani* under various conditions. It is worth noting that *Micrococcus radiodurans* given a dose of 2·5 Mrad is inactivated to the same extent as *Bacillus stearothermophilus* given the standard autoclaving procedure of 120°C for 20 minutes.

In the above, the effect of environment on sterilization doses has been neglected. Environmental factors can have a large effect on the radiosensitivity of micro-organisms and they have been recently reviewed by BRIDGES and HORNE[4]. The vegetative forms are more susceptible than spores to environmental modification and the two most important factors are oxygen tension and water content. Vegetative cells irradiated in anaerobic conditions require a three-fold greater dose for a given inactivation factor than cells irradiated in air[7]. Spores do not usually show a marked oxygen effect although it can be demonstrated under certain conditions[8]. The effect of water content is still uncertain. It has been claimed that vegetative cells are more resistant when dry. For spores, some workers failed to find any difference between the sensitivities of moist and dry spores[6,9] while others have reported that dry spores are the more sensitive[8,10]. More work is needed to correlate the various environmental factors discussed above.

Since spores may be more resistant when moist, and since marked oxygen effects have not been demonstrated with moist spores, we consider that the dose of 2·5 Mrad, calculated from data on moist spores, is probably the most useful estimate based on our present knowledge.

Sterilizing Dose in Practice

It is not enough, of course, to work out a sterilizing dose on a piece of paper, since practical tests must also be carried out on the various types of pharmaceutical or medical product concerned. A large number of such tests have been carried out, many of them so far unpublished. Others, such as the cooperative programme between the Technological Irradiation Group of the Isotope Research Division, the School of Pharmacy, University of London and the Association of British Pharmaceutical Industry, are in course of publication. From those which have been published, there is strong evidence that 2·5 Mrad is an adequate sterilizing

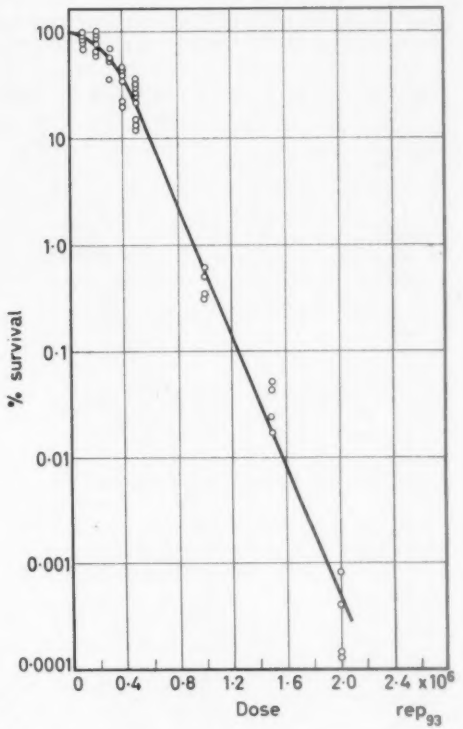

Figure 2. Effect of cathode rays on the survival of spores of Clostridium sporogenes irradiated in saline. (Fuld, Proctor, and Goldblith[29]. Courtesy Int. J. appl. Rad. Isot.)

* 1 Mrad = 10^6 rads

dose under most conditions. TARPLEY *et al.*[11] in 1952 found that between 1·86 and 2·54 Mrad was necessary to sterilize suspensions of 10^8 organisms per ml, and the most resistant organism was found to be *Clostridium sporogenes*. Several studies have been made on the sterilization of grafts of cadaver bone. BASSETT *et al*[12] found that 1·86 Mrad was sufficient to sterilize grafts contaminated with a wide range of bacteria. DE VRIES *et al.*[13] contaminated segments of dog humerus with a four day old culture of *Clostridium tetani* and two strains of *Clostridium botulinum*. After irradiation the contaminated bone was transferred to Brewer's thioglycolate media to determine which dosage level consistently produced sterile cultures. It was found that all bone receiving 1·86 Mrad and over was bacteriologically sterile.

Table 1. Calculated D values for various micro-organisms. (D = the dose necessary to reduce the initial population by 90 per cent.)

Organism	*Conditions*	*Calc. D value* (Mrad)	*Ref.*
Pseudomonas (green pigmented)	Moist, aerobic	0·005	33
Pseudomonas aeruginosa	dry, aerobic	0·013	30
Escherichia coli B/r	moist, aerobic	0·02	31
	moist, anaerobic	0·04	31
Micrococcus pyogenes v. aureus	moist, aerobic	0·016	35
	anaerobic	0·044	
Streptococcus faecalis 10C1	moist, aerobic	0·07	34
	anaerobic	0·15	34
Bacillus subtilis (vegetative) NCTC 2117	moist, aerobic	0·025	33
Bacillus subtilis (spores) NCTC 2116	moist, aerobic	0·19	6
	freeze-dried, aerobic	0·21	6
Bacillus thermoacidurans	moist, aerobic	0·12	32
Bacillus stearothermophilus	moist, aerobic	0·32	35
	moist, anerobic	0·42	35
Clostridium sporogenes	moist aerobic	0·5	29

These workers point out that a higher dose would be necessary if it were desired to eliminate viruses as well as bacteria. TURNER *et al.*[14] concluded that a dose of 0·93 Mrad of cathode rays would adequately sterilize sections of freeze-dried and frozen animal bone after contamination with *Staphylococcus aureus* (F.D.A.209). They also quote results of experiments with pure culture suspensions of various organisms. The most resistant was found to be *Cl. sporogenes* which needed 1·86 Mrad; *Salmonella typhimurium*, *Brucella abortis*, *Mycobacterium tuberculosis*, *Pseudomonas aeruginosa*, *Corynebacterium diphtheriae*, *Escherichia coli* and *Diplococcus pneumoniae* were among the more sensitive bacteria, needing less than 0·47 Mrad. BONET-MAURY and LORMAND[9], in a study of the sterilization of pharmaceuticals, found that gauzes sealed in plastic containers could be sterilized by 0·042 Mrad of Co^{60} gamma rays. If, however, they were initially contaminated with large quantities of *Bacillus subtilis*, 1·66 Mrad was normally needed, and in one instance 2·08 Mrad.

Recent Russian work[15] has included investigation of the possibilities of using gamma rays for sterilizing glassware and for treating waste materials from the bacteriological industry. The 'application of gamma rays to the preparation of nutrient media and to the production of corpuscular and chemical intestinal vaccines and diphtheria and tetanus toxoids' was also studied. In all these Russian experiments, even when manured soils containing particularly resistant spores were treated, a dose of 1·25 Mrad was found to be sufficient to ensure sterility.

Probably the most thorough practical investigation is that carried out by Ethicon Inc.[16] who tested 150 different species. They have chosen 2·5 Mrad as their sterilizing dose and claim that this is 40 per cent above the minimum needed to kill the most resistant micro-organisms.

It would seem justifiable from present knowledge at any rate, to consider 2·5 Mrad as a sterilizing dose with an adequate safety factor under most conditions.

Packaging

A sterilization process is quite valueless unless precautions are taken to prevent recontamination. It is most important that all articles being sterilized should be packaged in such a way that recontamination by bacteria is impossible. Radiation undoubtedly allows a much wider choice of materials to be used for packaging than any other sterilization method. All plastic films such as cellophane, cellulose acetate, polythene, nylon and of course metal foils are suitable at sterilization doses. The ideal packaging material should not only be impermeable to bacteria and have good heat-sealing properties, but should have good tear and impact strength and clarity for consumer appeal and should be cheap.

Few packaging materials have all these properties and the final choice would be determined by the application. This is illustrated by the work carried out by Ethicon Inc.[16] in the United States on a suitable packaging material for surgical cat-gut sutures to be sterilized by high-energy electrons. Many plastic films were first investigated but were found to be unsuitable because most of them were permeable to the fluids to be used inside and outside the package; 90 per cent *iso*propyl alcohol is used inside to keep the sutures pliable and the packages are stored in a jar of 97 per cent *iso*propyl alcohol and 1 per cent formaldehyde to maintain sterility of the outside of the packages. It is essential that formaldehyde should not penetrate through the package because this would damage the suture. An aluminium foil-plastic laminate was found to be the most suitable and the radiation-sterilized sutures are now marketed in packages made of this material.

It is sometimes advantageous to package certain items in double packs which allow an effective technique for maintaining sterility during the procedures of handling and opening; this is important as the package is exposed on its outer surface to recontamination after sterilization. It is sometimes argued that with double packaging there is always the danger of contaminating the inner container as it is withdrawn across the non-sterile cut edge of the outer film. If this is so the use of a 'dog-ear' type package is to be recommended as it is then possible to extract the sterilized item without touching the outside of the package.

Packaging is obviously a very important aspect of any sterilization method, and as such a wide range of materials is available for packaging when using the radiation technique, it is most important in considering this method of sterilization to investigate all possible types of packaging materials. Manufacturers may find that the additional cost of radiation processing can be offset by the advantages to be gained by improved quality in packaging and better customer appeal.

Applications

Biological materials, many of which are used clinically, are extremely difficult to sterilize by conventional heat methods. Recently several hospitals have set up arterial and bone banks so that these tissues can be available for immediate transplantation.

Supplying banks with sterile tissue is difficult because the material may be contaminated as a result of infection in the donor, during removal of the tissue at operation or autopsy, and also in subsequent storage. Any method whereby tissue could be obtained at the convenience of the pathologist without aseptic handling and then sterilized in suitable containers for storage would be of considerable benefit to these banks. MEEKER and GROSS[17] first suggested the use of ionizing radiation to sterilize arterial tissue and several workers have since used the technique for this purpose[18,19]. Unfortunately there has been considerable variation in the results obtained when arterial segments sterilized by radiation have been implanted in animals. There is no doubt that the tissue has been sterilized but mechanical properties such as tensile strength[20] have sometimes been altered so as to make the tissue unsuitable as grafting material. The variation that has resulted using this method suggests that considerable care must be taken in the preparative and radiation processes and these precautions rather detract from the use of radiation for this purpose. The recent development of plastic materials for arterial substitutes[21], however, may result in less demand for arterial tissue grafts in the future. These plastic substitutes are easily sterilized by radiation without damage; a *Terylene* arterial prosthesis, sterilized by gamma radiation, has recently been marketed by John Bell & Croyden Ltd, London.

Although most authorities would recommend the use of autograft bone, that is bone from the same individual, the taking of bone from another individual, either before or after death, and storing it for future use is to be preferred on the grounds of convenience. Ionizing radiation has been used very successfully by many workers[12,13,14] for sterilizing bone tissue and no serious disadvantage has been revealed in using this technique. In this country CHALMERS and his colleagues[22] have made a thorough investigation of various types of bone graft such as autograft, fresh homograft, frozen homograft, autoclaved homograft, demineralized homograft, deproteinized homograft, freeze-dried homograft and freeze-dried irradiated homograft. The authors found that there was no marked difference in the biological behaviour of any of the types of graft used, although the freeze-dried irradiated material was preferable on the grounds of sterility, availability and general convenience.

Absorbable surgical sutures, commonly known as cat-gut, have always been notoriously difficult to heat sterilize because of their proteinous nature. In order to minimize the heat denaturation of the sutures, it has been necessary before sterilizing to dehydrate them slowly in glass containers which are then aseptically filled with sterile fluid before final sealing. As previously mentioned, Ethicon Inc.[16] are now manufacturing cat-gut sutures in foil

packets sterilized by high-energy electrons at 2·5 Mrad. This method permits sterilization of the final sealed container on a continuous basis, which is preferable to the batch procedure, and results in minimal damage to the sutures. Non-absorbable sutures made from silk and nylon can also be sterilized by radiation.

In the pharmaceutical industry, sterilization of heat-labile preparations usually presents difficulties. Methods now in use include filtration for solutions, chemical disinfection, and fumigation with compounds such as ethylene oxide and formaldehyde. All these methods have limited application and must be used in combination with aseptic techniques which require careful control and can be expensive. Sterilization of heat-labile preparations by ionizing radiation in finished, sealed containers might therefore be of considerable benefit to the pharmaceutical industry.

It is not possible to predict the effect of radiation on the chemical and biological properties of particular pharmaceutical products; each one has to be carefully studied. In general products are more resistant in the solid or frozen states and more sensitive in dilute aqueous solution or suspension. This is illustrated by the effect of radiation on vitamins. A multivitamin preparation containing thiamine, riboflavin, pyridoxine, calcium pantothenate, nicotinamide, folic acid and vitamin B_{12} showed no change in activity after four years storage at 25°C when irradiated in a dry state but in aqueous solution some loss in activity was demonstrated[23]. Similarly, vitamin C can be radiation sterilized in the frozen state without loss of activity although in solution there is again some loss of activity. A loss in biological potency of 1·7 per cent and 13·0 per cent has also been shown in heparin irradiated at 2·5 Mrad as a freeze-dried powder and in solution, respectively[24].

Steroids appear to be fairly resistant to radiation. TARPLEY *et al.* irradiated aqueous suspensions of cortisone acetate with up to 12·7 Mrad and pregnenolone acetate with up to 6·0 Mrad and no changes could be detected in these compounds. FAZAKERLEY[25] has shown that powdered cortisone, prednisone and progesterone are stable to irradiation (6 to 18 Mrad) both in the presence and absence of air. Progesterone, however, developed a yellow colour and resinous odour at 10 Mrad. Ergosterol and calciferol were sensitive to radiation-induced oxidation but were relatively stable in the absence of oxygen. The antibiotics are also normally resistant to radiation damage. Potassium benzyl penicillin, streptomycin hydrochloride, aureomycin, chloramphenicol and terramycin have been irradiated at 1·8 Mrad in the dry state and no appreciable difference in the solubilities or potencies of the irradiated and unirradiated samples could be detected[26]. A slight change in colour was noted, however, in the irradiated samples of streptomycin and chloramphenicol. The effects of radiation (2·5 Mrad) on different forms of penicillin, streptomycin, polymixin and bacitracin have been determined and little change in potency has been detected although once again some of the solid products became slightly coloured and this colour persisted when they were dissolved[24]. Ergometrine maleate and morphine sulphate are stable to irradiation in the solid state but atropine sulphate and certain organometallic compounds are severely affected both in the solid state and in solution[24]. Hormones such as testosterone, oestradiol and pituitary hormone are stable to irradiation (0·8–1·1 Mrad)[27] but insulin and protamine zinc insulin are severely degraded at 2·5 Mrad[24]. Dry enzyme preparations are generally stable to radiation and two enzyme preparations, ficin and Maya protease, which are used clinically for wound debridement, have been successfully radiation sterilized on a routine basis[28].

It can be seen from the work quoted above that, although radiation cannot be used to sterilize all pharmaceutical products, this technique is nevertheless a practical and valuable addition to the other sterilization methods used in the pharmaceutical industry.

Cellulosic materials are not suitable for repeated sterilizations by radiation but cotton dressings, gauze, bandages and swabs can be successfully treated for use once only. Adhesive bandages can be sterilized if suitable adhesives are used and medicated dressings, impregnated with heat sensitive compounds, can only be treated successfully in this way. Many disposable items such as plastic syringes, needles, surgical blades, catheters, prostheses, surgical gloves, plastic tubing and petri dishes are all suitable for sterilization by radiation. A balloon catheter, sterilized by gamma radiation, is already marketed by William Warne & Co. Ltd, London.

There is no doubt that radiation processing is an effective method of sterilization and the above applications would appear to justify great confidence in its future.

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SURVEY

The Alert Controller

The bigger the power station, the greater the multiplicity of instruments displayed in the control room, and consequently the greater the number of built-in safety devices. This usually makes the onset of instability in the system rare, and may obviate an emergency altogether. In nuclear power stations, the situation reaches an extreme; everything is monitored—except the controlling engineer. He must be highly trained, highly skilled, alert and critical; but, being human, he gets bored if he has no decisions to make because his plant is automatically controlled. For an estimated term of twenty years, routines are required which will help to keep the controller's critical faculties at their most efficient and it was to advise on the 'human engineering' aspects at the Sizewell installation that Dr J. H. ELY and his colleagues from Dunlap and Associates Inc., of Stamford, Conn., came to the U.K. Their report was presented recently to representatives of the General Electric Company, the Central Electricity Generating Board, the United Kingdom Atomic Energy Authority, the Department of Scientific and Industrial Research and the Admiralty.

Dr Ely stated that this was their first assignment in the nuclear engineering field. They approached their examination bearing in mind the sort of things man does well, and making allowances for national characteristics. The controlling engineer has two main functions: he must ensure safe operation of the plant, and he must make system operation more effective. He must take corrective action early enough to prevent the station going off-load when only minor instabilities develop, at the same time ensuring that precautions are taken to prevent the equipment being damaged by overloads. He should be assisted in his interpretation of instrument behaviour, to induce him to make the right decision. Therefore instruments have been arranged, panel by panel, so that all those of the same kind appear on one level and those of another kind appear on a different level; their scales are adjusted so that under normal operating conditions the needles are vertical and it is immediately obvious to the human eye, tutored or untutored, if one needle starts to behave erratically.

A man may stand if he gets excited—so control knobs are arranged to enable him to make the same movement whether he sits or stands at the control desk. Men are poor monitors—just watching needles is boring. Much of the monitoring can be carried out automatically and it has been suggested that the controller's ensuing boredom can be counteracted by arranging a regular rotation of jobs of comparable responsibility.

There should be three men in the control room as a rule—social contact helps to keep them all alert—

but one must be in charge, and should behave as one man with six hands if the team is well chosen and properly trained.

Provision of a station computer would bring advantages of prediction, and could be used in training new teams, while the station physicist would always require it for evaluation of records. Recommendations also cover restricted use of audible warnings, changing of habit patterns, use of manual control as a back-up system for, say, fifteen minutes in each hour, and an outline was given of qualities, training and abilities of personnel as a guide to those choosing staff for these projects.

Gas in Industry

The Gas Council are anxious to show the marked advantages of gas for industrial use and for this purpose they organized two 'Gas at Work in Industry' exhibitions, one of which took place in London from 1-12 March and the other in Harrogate from 28 March to 1 April. These exhibitions were designed to point out those fields where gas is more convenient, economical and labour-saving than other fuels. The main advantages of gas are its flexibility and the fact that it is easy to maintain accurate temperature control. These features are of great benefit in such industrial applications as glass-making, metal melting, water and space heating, gear hardening, die casting, baking, catering *etc.* It is claimed that gas is used in some 4000 different processes in about 1000 different industries.

The advantages of gas in industry, and examples of its widespread applications, have also been demonstrated in press visits to various factories. The extensive use of gas in glass manufacturing, glass working, electronics and wire manufacturing was shown at a recent visit to two of Mullards' factories, one at Simonstone, where television tubes are manufactured, and the other at Blackburn where glass, radio valves, and tungsten and molybdenum wire are made. At the Blackburn factory glass is manufactured in very large gas-fired furnaces at temperatures of 1400–1500°C: over fourteen thousand miles of glass tubing is produced every year. This tubing is used for radio valves, and in both the Blackburn and Simonstone factories there were demonstrations of the way in which gas–air jets are used on rotary machines to pre-heat glass components which are finally welded together using oxy-coal gas jets; the faceplate and cone (or back) of the television tubes are joined by an electric arc struck through gas flames, bringing the edges of the components up to melting point to make a perfect seal (see *Figure 1*). To ensure even heating and to prevent strain in the glass the gas jets automatically follow the contour of the faceplate as the bulb rotates.

Gas also plays an important part in the making of fine tungsten and molybdenum wire at the Blackburn works. For example, finely ground and chemically purified tungsten (or molybdenum) oxide powder is reduced in a hydrogen atmosphere at 900°C; special

Figure 1. One of the automatic machines for welding TV Tube faceplates to the neck and cone assemblies

additives are introduced to control the crystal structure and the powder is compressed into bars which are sintered by again heating in a hydrogen atmosphere and then passing an electric current of 2000 to 3000 amps through them. The wire is then formed by successive stages of heating to white heat over an open gas flame and, in the early stages, hammering out the wire into rods and later drawing it out through dies to finer and finer threads. The finest wire produced at Blackburn has a diameter of 5 microns.

Electronic Editor

An I.B.M. computer has recently saved Cornell University Press editorial staff months, or even years, of preparing, collating and editing. Under the guidance of the editor, Professor PARRISH of Cornell University English department, and his assistants, a 965 page concordance to the poems of Matthew Arnold, containing the occurrences of 101,097 words of Arnold's vocabulary and about 50,000 references was sorted out by the computer in a matter of thirty-eight hours.

BOOK REVIEWS

Radioisotopes for Industry

R. S. ROCHLIN and W. W. SCHULTZ

(ix+190 pp; 7½ in. by 5 in.)

New York: Reinhold Publishing Corporation;
London: Chapman and Hall. $4·75, 38*s*

THIS little book provides an excellent review of the uses of radioactive isotopes as an aid to production in a wide range of industries. It is clearly written, presents facts and figures in an interesting and stimulating fashion, and offers interesting and useful reading to the works or plant manager, as well as the technologist.

The subject is presented in a logical manner, beginning with an introductory chapter which emphasizes the economic advantages to be gained in industry from the use of isotopes by quoting an estimate of the United States Atomic Energy Commission Report to Congress (1957) that the industrial use of radioisotopes in the United States was making possible a gross saving of nearly 500,000,000 dollars a year in such processes as cigarette making; metal, rubber, plastic, and paper gauging; radiographic inspection; mineral and oil prospecting and processing; tool and machine wear study; material flow measurement; leak detection, *etc.* The following eleven chapters discuss specific fields of use, including in each some well chosen examples of particular uses. As well as including well-known examples of isotope usage in industry, all the chapters include quite a number of very interesting but lesser known uses which stimulate the reader into thinking about potential applications in his own field of activity. For example, Chapter 2 on the subject of non-contact gauging, *e.g.* of paper and foils, refers to a method of measuring the thickness of ink on a lithographic printing roller by plating the roll with radioactive nickel beneath a flash of copper. A detector then responds to changes in ink thickness in the range 3–7 microns. Chapter 4, in surveying the use of isotopes in the measurement of mechanical wear, includes an interesting technique by which measurements can be made of the relative rates of wear of two rings on a piston in an internal combustion engine by labelling the rings with two different radioactive isotopes obtained on irradiation of iron and then selective detection. Chapter 5 discusses activation techniques for study of wear, measurement of trace impurities, or metal analysis by activating the sample with neutrons to make impurities radioactive and detectable to such an extent that in favourable circumstances one part in 10^{14} can be estimated. Chapter 6 on tracer techniques in research and development mentions their use in studying washing processes and detergent efficiencies for soil removal. Chapter 7 discusses uses in manufacturing processes, such as dissipation of static electrical charges, checking the proper mixing of constituents, the induction of chemical reaction in forming long chain sulphonic acids for improved detergents, and several techniques for flow measurement. Chapter 8 highlights uses in leak detection, *e.g.*, from buried pipes, *etc.* Chapter 9 on miscellaneous applications describes how the protein content of cereal grain can be measured by its nitrogen content, which is assessed by irradiation with neutrons and measurement of the consequent high energy gamma radiation due to the nitrogen. Among possible new uses are suggested the measurement of the rates of oxidation of paper and thus the rate of deterioration by measurement of the CO_2 evolved using a labelled carbon in the paper. Chapters 10, 11 and 12 discuss equipment available, facilities for training personnel in the United States—noting that 68 colleges throughout the U.S.A. offer training courses in this subject, protection from radiation hazards, and a brief review of future possibilities for extended use of isotopes.

Proper attention is given to the economic benefits of isotope usage in industry. For example, in Chapter 3 mention is made that the standards of the American Society of Mechanical Engineers allow a 12 per cent thinner steel to be used for pressure vessels if the material has been radiographed to detect defects. In Chapter 4 it is pointed out that in the planning of a nineteen mile long pipeline to carry a slurry severe corrosion was anticipated by laboratory studies with isotopes, which enabled corrective action to be taken in good time and this resulted in an estimated saving of 1,800,000 dollars.

Throughout the book many useful references to the literature are given and there is a very good bibliography appendix which will enable the reader to follow up in detail any of the very many applications discussed throughout the text. Other useful appendices given include tables of radioactive isotopes available and of isotopes which can be activated by thermal neutrons. There is also a brief but useful appendix on the technical aspects of radioactivity.

Altogether this is a book which well justifies the attention of a very wide section of readers concerned with applied science and industrial practice. S.S.C.

The Molecular Basis of Evolution

C. B. ANFINSEN

(xiii+228 pp; 9¼ in. by 6 in.)

New York: John Wiley and Sons Inc. 56*s*

THE title of this book is perhaps a misnomer since, in order to be able to evolve, an organism must have some kind of genetic variance, and thus the molecular basis of evolution must essentially be the molecular basis of genetics as shown in this book. Since Dr ANFINSEN is not prepared to speculate unless there is extremely good ground for speculation, he is unable to say much about the relationship between the known species differences in proteins and the grosser types of evolution such as seen in the development of bone structure. There are chapters dealing with genetics and the chemistry of genes, proteins from the standpoint of structure, biological activity and genetic control of synthesis, and the general relationship between genes and proteins with a rather brief summary of some of the evolutionary aspects of proteins.

The chapters dealing with the structure of proteins are clear and concise accounts of the progress which has been

made in the last few years, and to which Dr ANFINSEN has contributed no small part, and are readily understood by the non-specialist. The chapters on genetics are also well written, especially those dealing with bacteriophages, but perhaps they suffer from the fact that Dr ANFINSEN is not a geneticist which allows some small points of description to be misleading. For instance when describing the selection of streptomycin-resistant *pneumococci*, the organism is said to '. . . have acquired, by a chance mutation . . .' when it was plain from the previous description that the genetic mutants must already have been present in the population of *pneumococci* before treatment with streptomycin in order that there should have been survivors which were resistant, and not that the mutations had occurred in response to the treatment with streptomycin as the text would imply.

In dealing with the structure of proteins and the species differences in proteins the concept of an ' active centre ' containing the only physiologically important part of the molecule has been given too much prominence. Certainly it is true that there are parts of a protein molecule which are essential for such things as enzyme activity, and that they are invariant, or change very little, in the proteins of different species, but it is dangerous to state from these premises that the rest of the molecule is inessential, or even of less importance, without first examining the kind of amino acid change which is involved in species differentiation and the rôle of the protein *in vivo*. For example when dealing with insulin it is suggested, since only three of the amino acids present in the disulphide loop of the A chain and no others outside this area differ in the insulins from different species, that they '. . . are not particularly crucial ones from the standpoint of normal activity '. However upon examination of the type of amino acid changes found in the six insulins listed it is found that alanine changes to threonine, serine to glycine, and valine to *iso*leucine and threonine in different combinations, showing that the type of amino acid change is quite severely limited; and that the limitation may be governed by structural or other factors, and that perhaps any other type of amino acid change has been eliminated by ' natural selection '. The differences found in species related proteins may well explain the known differences in immunological specificity, and it may be that the factors which determine the immunological specificity of a protein will help to place it in its correct position in the cell, and that any differences in the immunological specificity could alter the cell enough to account for the gradual evolution of grosser phenotypic characters.

This is a small book covering a wide field so that it cannot be expected to be complete. Where there are omissions there are adequate general references, and certainly those not familiar with genetics would be well advised to follow them up.

The lay-out of the book is up to the best American standards. It is a book which will stimulate all of those who are interested in what is perhaps one of the most exciting fields in present day biology, whether they are biochemists or not. J.A.H.

Ion Exchange. A Laboratory Manual

J. E. SALMON and D. K. HALE

(*vii+136 pp; 8¾ in. by 5½ in.*)

London: Butterworths Scientific Publications; New York: Academic Press. $5, 25*s*

ALTHOUGH publications concerning ion exchangers and their possible applications have multiplied spectacularly in recent years, there are relatively few books on the subject. None sets out detailed practical instructions for the numerous laboratory applications. The sub-title of SALMON and HALE's book thus leads one to expect a useful contribution to ion-exchange literature. Moreover, the preface implies that fresh ground is also broken by stating the book to be suitable for use in colleges and schools. Unfortunately, the latter consideration seems to have led the authors to give an over-simplified account of ion-exchange theory, and in consequence opportunities are missed for instructions which are deductive and precise rather than just simple. The insistence on the term ' absorption of ions ' in place of ' exchange ', ' replacement ' or a similar phrase having the appropriate physical meaning illustrates this point. Also, the selectivity coefficient has been derived most arbitrarily, referring to the law of mass action as an afterthought, yet a few pages later employing this law (use of which, incidentally, would give the student a better insight into the development of ion-exchange concepts, especially if presented in conjunction with alternative derivations of the equilibrium relationship). In passing, the reviewer would like to record his strong objection to such new terminology as ' practical or " stoichiometric relative affinity coefficient " (*sic*) '. An illuminating and pellucid chapter on ion-exchange resin preparation occupies an eighth of the book, but it is questionable whether such an extensive section is justified in a ' laboratory manual '. In this day of abundant supply of a variety of such materials from numerous manufacturers very few users indeed are likely to be called upon to prepare exchangers.

As might be expected the *forte* of this book is in the parts dealing with laboratory applications, though a few ambiguities also intrude here. Thus, for instance, it is not clear what is meant by ' exclusion of strong electrolytes '; neither of the phenomena, resulting from the size (sieve effect) and charge (co-ion exclusion) of the ion, generally referred to as exclusion seems to be involved. The small-type notes which follow many of the experiments described are not merely footnotes but a mine of incidental information, indicating that good use has been made of the authors' background of practical experience. Occasionally, however, they contain information which if not taken into consideration could invalidate the experiment. Thus, footnote *c* of experiment *2a*, illustrating the non-equilibrium, direct titration method of capacity determination, warns of the necessity to allow time for the exchange to be completed. Though not stated, this is particularly crucial if a ' weak ' exchanger is used. The concluding sections of each experimental chapter warrant commendation, giving a succinct and reasonably critical appraisal.

To conclude, this book represents a brave attempt to provide a foundation which would allow the technique of ion-exchange to be included in teaching curricula, as well as a manual for scientists wishing to employ the relatively novel yet powerful experimental tool which ion exchangers have provided. As the field covered is an expanding one, new editions should be forthcoming at comparatively short intervals and it is hoped the opportunity thus afforded will be used to eliminate certain less satisfactory aspects of what is on the whole a commendable book. A.O.J.

Physico-Chemical Measurements at High Temperatures

J. O'M. Bockris, J. L. White, J. D. Mackenzie (*Eds*)

(*viii+394 pp; 10 in. by 6½ in.*)

London: Butterworth's Scientific Publications. 75*s*

It is almost superfluous to stress the increasing importance of high temperature technology in this day and age. Experience in this field of work is widely scattered throughout the literature, and the book attempts a carefully considered survey of it. Nineteen experts have contributed, the chapters dealing with means of attaining, controlling, and measuring temperature; stability of refractory materials; phase and chemical equilibria; calorimetry; liquid densitometry; surface tension; vapour pressure; electrochemical measurements; scattering and absorption of visible light in fused salts; ultrasonic velocity measurements; measurement of diffusivity in liquid systems; and viscometry. There are also seven appendices of data which should be invaluable to the apparatus designer.

The editors are to be congratulated on bringing a measure of coherence into the resulting book. It would be impossible to treat the subject exhaustively in a volume of this size and, obviously, original papers and other specialist works must be consulted for details. Copious references are provided to guide the reader, *e.g.*, temperature measurement is covered in 35 pages, but there are 187 references for this chapter alone! The book is well produced with clear diagrams, but it is a pity that authors' initials have been omitted throughout. Misprints seem to be few and obvious, so that the reader is unlikely to be misled.

This is definitely a book for the experimentalist, particularly one already active or contemplating activity in this field. The theoretician will be dissatisfied with it—unless he wants to find out how the experiments are done. V. R.

Ammonia Manufacture and Uses

A. J. Harding

Electrolytic Manufacture of Chemicals from Salt

D. W. F. Hardie

(*xii+41 and xii+73 pp; 8¾ in. by 5½ in.*)

London: Oxford University Press. 7*s* 6*d* and 6*s* 6*d*

These books, the 2nd and 3rd in the series, are aimed to bridge the gap between classroom chemistry and industrial practice and in this they succeed admirably. A very full account has been presented, step-wise and with clarity. Fundamental physico-chemical principles are simply expounded and applied to every reaction encountered and, in conjunction with economics, lead on to operating conditions. Energy relationships are rightly stressed and economic factors readily comprehended. The statistics are informative and the photographs bring reality. They might be thought to attempt too much and cause mental indigestion with surfeit of figures; certainly the danger is there.

Undoubtedly if these books are in school science libraries they will be read and provide invaluable contact with industry, but they are capable of imparting a more specialized knowledge than the majority of readers will need to acquire. Teachers can profit as well as pupils, for they will also find authoritative and recent information not easily available elsewhere. T.A.G.S.

Lectures on Nuclear Theory

L. Landau and Ya. Smorodinsky

(*vii+108 pp; 9¼ in. by 6 in.*)

New York: Plenum Press, Inc.; London: Chapman and Hall Ltd, 1958. 85·25, 45*s*

During 1954 the distinguished Russian theoretical physicist L. D. Landau gave a course of ten lectures on Nuclear Theory, primarily for an audience of experimental physicists. These were edited by Ya. Smorodinsky and published in Russian, and subsequently translated into English by Consultants Bureau Inc. in 1958; they have now been reprinted.

The aim of the lectures was to give an indication of the main topics, and methods by which order can be perceived, in what has become one of the largest fields of physics. Throughout, the emphasis is on physical ideas, and there is little in the way of detailed working out of their consequences. Persons with no previous knowledge of nuclear physics will learn little of value here, though they may well come away with the illusion of knowledge. Experimental nuclear physicists, actively working in some branch of nuclear physics, will probably find it stimulating, in spite of its many defects. It will do little to give them the means of understanding deep theoretical points for themselves, but it will show them the broad lines along which theorists have been looking at nuclear phenomena. By its refreshing insistence on the fact that there is no adequate theory of this, that or the other aspect of phenomena, it will keep up their morale, should they be feeling bogged down by the technical difficulties of their own work.

Its main defect is that it is already out of date. This is most serious in the lectures on nucleon–nucleon scattering, and on nucleon–pion interactions, which discuss 'recent' experimental data, where experimental progress in Russia and the United States has been very rapid, and information is now very much more complete. The section on symmetry principles (lecture 9) is very interesting, though having been written before the discovery of parity nonconservation, a modern version would say some of the things differently. The book is a little careless in places, giving the impression that some of the lectures

were inadequately prepared in points of detail (which could have been rectified in the editing, but have not). The translation would have been better if it had been done by somebody with a working knowledge of the subject. Frequently there are completely erroneous statements which can be rectified by simple transposition of a few words—clearly the result of mistranslation. The type is very small, and makes reading in a poor light difficult.

This book is recommended to theoretical physicists who plan to give a course of lectures to their experimental colleagues, and whose institution can afford the high price. They will find it a very stimulating model for giving a set of lectures in a field so vast that selection of material is the major difficulty—and a proof that one can get physical ideas across with the minimum of mathematics. M.H.L.P.

Nuclear Reactor Materials

B. R. T. FROST and M. B. WALDRON

(*vii+79 pp; 8½ in. by 5¾ in.*)

London: Temple Press Ltd. 12*s* 6*d*

THE book is one of a series on nuclear engineering under the general editorship of W. K. MANSFIELD. The titles of the other copies which have been published so far are Elementary Nuclear Physics; Nuclear Reactor Theory; Reactor Heat Transfer; Nuclear Reactor Shielding; Nuclear Reactor Control and Instrumentation; Steam Cycles for Nuclear Power Plant; Nuclear Reactor Materials; Nuclear Radiation Measurement and Nuclear Reactor Optimization. The present monograph is based on lectures by the staff of the Metallurgy Division at Harwell to students in the Department of Nuclear Engineering, Queen Mary College, London. Chapter headings are Theoretical Metallurgy; Structural Materials; Fuel Materials; Liquid Metals; Ceramics and Metal–Ceramic Mixtures as Reactor Materials and Corrosion. Such monographs at prices which are modest by present day standards are obviously of very great use to students beginning the study of these subjects. The treatment seems to be both careful and as thorough as can be expected, given at the level of the reader for whom they are intended. G.K.T.C.

Process Integration and Instrumentation

Electricity and Productivity Series, No. 8

(*xx+203 pp; 8¾ in. by 5¾ in.*)

London: Electrical Development Association. 8*s* 6*d*

WITH the increase in the use of the automatic control of processes it is important for the user and designer to be able to understand in detail the capabilities of many electrical instruments, electronic and otherwise, and also of a major assembly of control instruments and tools treated as a single unit. Process integration is defined as ' breaking down operations into simple stages, examining each one critically, and making fundamental alterations or adding devices which will make these operations work automatically as a whole unit '. The present volume is one of a series devoted to electricity and productivity and deals with the general field of automatic control, indicating the many devices available for various industrial functions, grouped under such headings as sensing, computers, electrical and electronic links.

The range of devices and industrial systems described is wide and up-to-date, and the book should serve as a useful introduction or even reference work to production engineers or to executives with a technical background. One feature of the book is the large number of excellent photographs of equipments and devices, and the list of manufacturers to whom acknowledgment is made provides a useful initial list of suppliers of control equipment. C.A.H.

Atomic Age Physics

N. SEMAT and H. E. WHITE

(*230 pp; 8 in. by 5¼ in.*)

New York: Rinehart & Company, Inc; London: Chapman & Hall. $2, 16*s*

PROFESSOR WHITE is well known not only as an author of standard texts in physics but in recent years as publicizer of teaching methods both by his preparation of cine film and his appearances on American television. Professor SEMAT is the author of a number of well known student's texts published in America.

This little book of 230 pages was prepared for use with a television course presented by the N.B.C. and closely follows the second half of this television course. As a condensed survey of atomic physics it is excellent. One only hopes that the television audience could keep up! The diagrams are very striking, they include portraits of distinguished physicists. Certainly it has done much to stimulate the reviewer's ideas of precisely what elementary students can be expected to know. G.K.T.C.

Ion Exchange Resins

THE BRITISH DRUG HOUSES LTD

(*64 pp; 8½ in. by 5½in.*)

Poole: The British Drug Houses Ltd

THIS little publication of sixty-four pages is the fourth edition of the British Drug Houses booklet on this subject. It gives details of the physical properties in this important class of materials and indeed contains full details of all resins in the *Amberlite* and *Permutit* ranges. There is a table containing the potential and recommended applications of the various resins, and a bibliography. G.K.T.C.

Journal of Electroanalytical Chemistry: Vol. 1, No. 1. August 1959

G. CHARLOT, J. O'M. BOCKRIS and C. N. REILLEY (*Ed.*)

(*100 pp; 9½ in. by 6½ in.*)

Amsterdam: Elsevier Publishing Company. Dft. 66·50, $17·50, £6 5*s* 0*d*, per volume

THE Journal of Electroanalytical Chemistry is now being published. The first number of the first volume was published in August 1959. This is an international journal dealing with all aspects of electroanalytical chemistry, including fundamental electrochemistry. G.K.T.C.

Methods for the Determination of Toxic Substances in Air

J. C. GAGE, N. STRAFFORD and R. TRUHAUT

(65 pp; 10 in. by 6¼ in.)

London: Butterworths Scientific Publications, 1959. 30*s*

IN A general introduction, the principles and techniques of sampling gases vapours and dusts are given together with the reasons which led to the choice of the particular methods described. The introduction also contains a useful list of references. This is followed by a description of analytical methods for some twenty materials including Ammonia, Chlorine, Methanol, Nitrobenzene and Chromate dust—the only solid material included. For each material the Maximum Allowable Concentration for continuous eight-hour per day exposure is given.

The maintenance of health in Industry is a subject of great and ever growing importance, and the present collection is the beginning of a most welcome and authoritative work in this field. G. N.

LETTER TO THE EDITOR

X-Ray Scattering of Carbon Black

SIR,

Carbons formed by thermal decomposition of organic substances at moderate temperatures consist of very poorly crystalline material. Graphitization of these carbons by heat-treatment involves crystallite growth and structural development and these effects can be studied by X-ray diffraction. Ultimate development is determined by many factors including particle size, porosity, cross-linkages, impurity, and orientation effects.

Information concerning particle size and porosity (in the sub-micron range) can be deduced from X-ray scattering at angles close to the incident X-ray beam. The technique of small-angle X-ray scattering is well established[1] and has received a number of applications in the study of carbon[2-8]. However, one of the serious limitations in small-angle scattering work is the acknowledged ambiguity in interpretation which can arise from the reciprocal (Babinet) effect of 'particles' and holes in producing scattering effects.

The present investigation of a carbon has provided a very real demonstration of correlation between (*1*) scattering effects interpreted in this instance as porosity, and (*2*) porosity measured by helium displacement. The carbon was Magecol–555 which is a colour-grade lampblack and has the distinction of having been formed at a temperature well below 1000°C. Samples of this black had been calcined at various temperatures up to 2000°C and data on density by helium displacement (ρ_{He}) and total gas content were available[9]. Using copper K_α radiation and a Philips (PW1050) Counter Diffractometer in the conventional para-focusing orientation, traces were obtained in the angular range 3–20°2θ for each member of the calcination series. (3°2θ was the instrumental cut-off for the 1/6° goniometer slits used: smaller slits to reduce the angle of cut-off resulted in prohibitively small counting-rates.) In the range recorded, each black gave a rising level of scattering with decreasing angle, but the magnitude of the scattering was different for each sample.

With very slight misalignment of the goniometer to allow a larger volume of sample to contribute to the measurements, maxima in the scattering curves were observed near the instrumental cut-off at 3°2θ: the level of the scattering was also increased. Typical curves for six calcination temperatures are shown in *Figure 1*. Exact positions and intensities of the maxima were critically dependent on degree of misalignment. With any specific goniometer alignment, including the correctly aligned position, the scattering curves obtained for the untreated black and all samples calcined at temperatures below 1000°C differed in intensity but not in general shape: in settings where peaks were detected, they were observed at smaller angles for calcination temperatures exceeding 1000°C (*Figure 1*). Simple tests with filters, and the examination of control specimens of diamond,

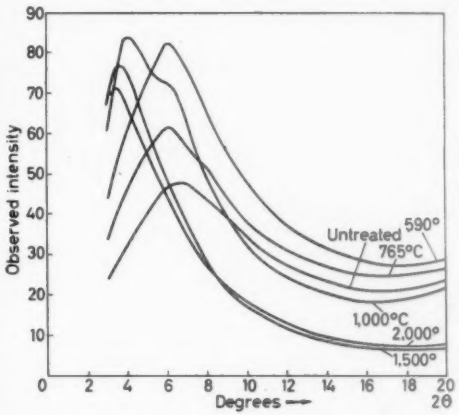

Figure 1. Typical X-ray scattering curves for Magecol-555 black calcined at temperatures up to 2000°C. (1/6° divergence and scatter slits, 0·2° receiving slit; Ni-filtered Cu radiation 40 kV 14 mA: Geiger counter; mass of each specimen 0·07g)

natural graphite, and gum tragacanth (for which the specimen weight and absorption were effectively the same as for the carbon black specimen) established that the effects were 'real'; repeatability was also very satisfactory.

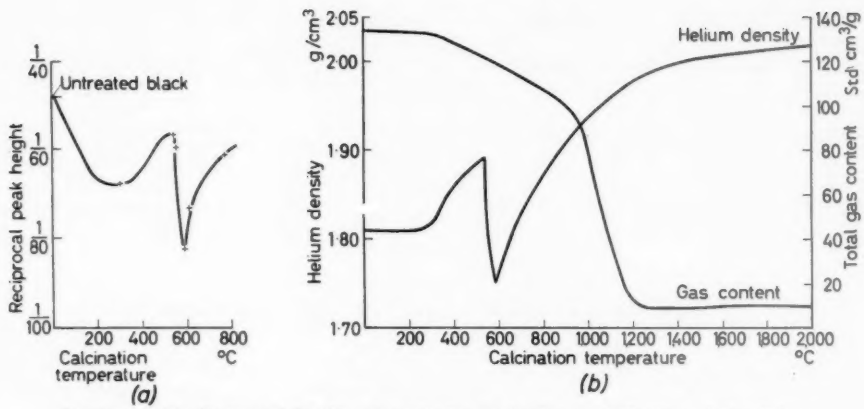

Figure 2. (*a*) *Reciprocal heights of scattering peaks* (*as an indication of density*) *vs. temperature of calcination.* (*b*) *Density* (*by helium displacement*) *and total gas content vs. temperature of calcination*

These effects and the positions of the peaks cannot be explained on the assumption that the individual crystallites are the units of homogeneous density responsible for the scattering: over the temperature range involved the crystallite size changes[10] from *c.* 15 Å to *c.* 70 Å and there are no discontinuities in the growth rate. Similarly the effects do not arise from the particles of black acting as the scattering units: electron microscope data shows[9] that the particle size is fairly constant at *c.* 700 Å.

The striking correlation of the scattering data with porosity deduced from measurement of density (by helium displacement) however, is illustrated in *Figure 2.* Using the reciprocal peak heights of the scattering curves for temperatures up to 765°C as a measure of density on an arbitrary scale (*Figure 2a*), there is close similarity to the ' helium density ' curve (*Figure 2b*). For this empirical comparison, it was not necessary to apply any corrections for the usual angle factors (*e.g.* Lorenz-polarization, atomic scattering factor, *etc.*) since a constant weight of specimen was used throughout and the peaks for this part of the temperature range were at a constant angle. The evidence for a change in angular distribution of scattering with calcination above 1000°C prohibits the comparison with ρ_{He} from being extended to include the higher temperature range. Below 1000°C, the correlation between the (deduced) porosity and ρ_{He} suggests that the pores are inaccessible to helium.

From the scattering measurements it would seem that there are fewer pores in the untreated material than in the material calcined at 300°C (*Figure 2a*), although ρ_{He} is the same for both samples (*Figure 2b*). This, the only apparent discrepancy, may be due to the presence of a much larger proportion of non-organized low-density material in the untreated black.

An interpretation that the displacement of the scattering maxima to smaller angles for temperatures of calcination above 1000°C corresponds to growth of pores, is supported by the evidence that at about 1000°C there is a sudden increase in the rate of gas evolution (*Figure 2b*) which would be expected to increase the pore size. Moreover, increased ρ_{He} above 1000°C implies, reasonably, that the pores are now accessible to helium.

These various observations illustrate the amount of information which under favourable conditions can apparently be obtained from x-ray scattering effects.

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B. P. COOK

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Wembley, England. *10th February, 1960*

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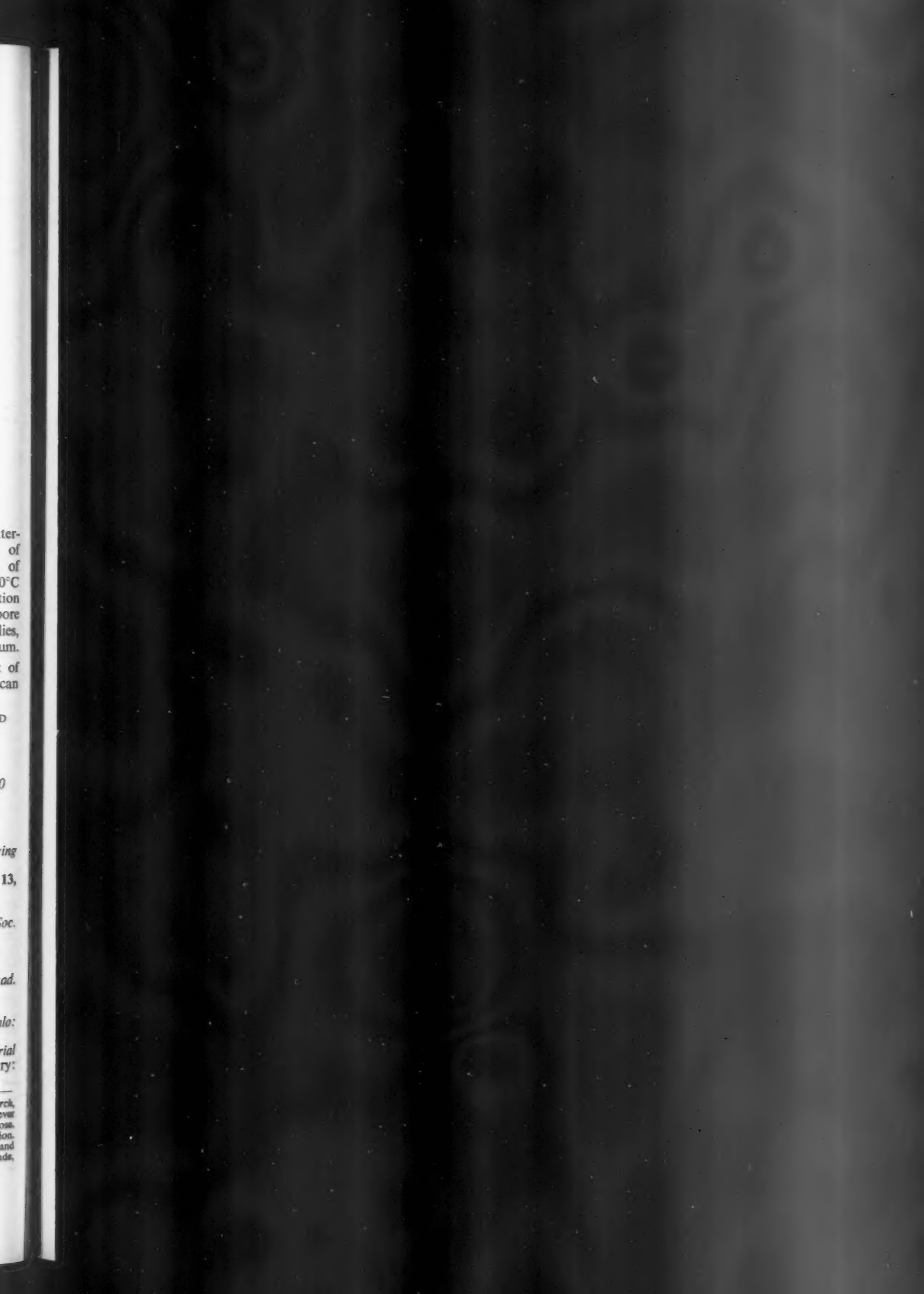
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